

Risk-Based Decision-Making for Assessing Petroleum Impacts at Exploration and Production Sites

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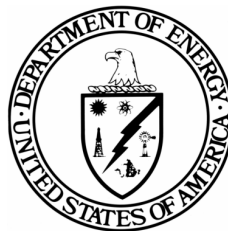
**RISK-BASED DECISION-MAKING FOR ASSESSING
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EDITED BY: MCMILLEN, MAGAW, CAROVILLANO

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Preface

Remarkable changes in the approach used for protection of human health and the environment in the United States have occurred over the past 30 years. During the period from the early 1970's through the early 1990's, setting priorities on which environmental problems were important was not an issue. The problems and apparent culprits were obvious. The public and regulatory agencies agreed on the severity of environmental problems and what was needed to correct them. As a result, legislation was passed, regulations were promulgated, and efforts and resources were focused on obvious pollution control problems. Meeting these regulatory needs became the primary goal of municipalities and industries during this period.

Over time, the increasing number of environmental laws and regulations, as well as the increasing complexity of environmental problems, began to strain the resources of regulatory agencies, municipalities, and industry. Interest increased in identifying and considering different approaches for environmental protection. As early as the mid-1980's, it was recognized that approaches other than the compliance, command, and control approach for environmental protection were needed. While he was Administrator of the United States Environmental Protection Agency (USEPA) in the mid-1980's, William Ruckelshaus attempted to introduce the concepts of risk assessment and risk management into the USEPA decision-making process. Attempts also were made to distinguish between the two concepts.

In 1990, then USEPA Administrator William Reilly called for a national debate on national directions and policies for environmental protection. What stimulated that call was the 1990 USEPA Science Advisory Board Report, "Reducing Risk: Setting Priorities and Strategies for Environmental Protection." Among the many recommendations in that report was one that recommended targeting environmental protection efforts on the basis of environmental risk and risk reduction opportunities. Also recommended was the use of risk-based priorities in environmental planning and budgeting.

Winston Churchill, at a critical turning point in World War II, stated, "This is not the end. It is not even the beginning of the end. But it is, perhaps the end of the beginning." Unrecognized at the time, but obvious in hindsight, is the fact that, in the United States, about the year 1990 was the "end of the beginning" period of environmental protection in which government laws and regulations were considered as the best approach for such protection. From the early 1990's, environmental protection efforts increasingly have focused on risk assessment and risk management approaches.

It is clear that the compliance, command, and control approach that dominated regulatory enforcement policy since the 1970's is no longer the predominant driver of the profession and the environmental industry. It also is clear that we will see a continuing firm regulatory baseline, with strong enforcement to define the floor for environmental progress and sustain the legal mechanism for penalizing environmental violators. Thus, we will have both a strong regulatory program and an increasing emphasis on risk assessment and risk management approaches for environmental protection.

From the initial efforts in the 1980's, risk-based evaluations and decisions have become an important component of efforts to protect human health and the environment. The information in Chapter 1 of this document provides an excellent summary of the development of the risk-based decision-making (RBDM) process and the current state of its use, particularly for sites with contaminated soils. Thus, Chapter 1 is an overview of the important concepts and incremental growth of RBDM in this second and important phase of environmental protection.

A value of the RBDM process is that each site is treated individually and that the remedial measures result in cleanup levels that are environmentally acceptable for the given site characteristics and anticipated land use. For situations where there are groups of sites, the RBDM process allows resources to be focused on sites or areas that have greater environmental concerns. The RBDM process also allows regulations to incorporate reasonable but conservative "Tier 1" screening levels. This avoids the use of overly conservative approaches such as achieving background concentrations or utilizing technologies deemed "best available" by non-risk based criteria.

Utilization of the RBDM process:

- Recognizes the differences of each site,
- Encourages owner rather than regulatory-led activities,
- Uses and integrates human and ecological risk-based knowledge, and
- Provides a focus on achieving site-specific environmental protection.

For sites with contaminated soils, the RBDM process results in achieving an environmentally protective endpoint, i.e., a concentration of a chemical in such soils below which there is no expected adverse effect to human health and the environment.

The increased emphasis on RBDM has required greater knowledge of factors that affect chemical release, transport, exposure, and general availability in the environment. In turn, this need triggered scientific, pilot scale, and field evaluations that have provided such knowledge.

In terms of risk-based assessments, for sites with contaminated soils, some of the important scientific and technical knowledge that has resulted in the past 10 years includes the following:

- The fact that a chemical, such as a petroleum hydrocarbon, can be measured in a soil says nothing about the actual risk that that chemical may pose.
- Not all chemicals in a soil are easily released and leachable.
- It is possible to allow some chemicals to remain at a site and still be protective of human health and the environment.
- Reasonable information is available to evaluate site-specific risks of chemicals in a soil.
- It is not mass removal of chemicals at a site, but rather risk reduction related to the expected use of the site that is important.
- Some concentrations of anthropogenic chemicals in a soil may have limited availability.
- The site remediation question is not “how much contamination can be cleaned up,” but rather “how much contamination should be cleaned up.”
- Information about the chemical release in a soil and chemical exposure to a receptor is important in the RBDM process.
- Natural attenuation of chemicals such as petroleum hydrocarbons does occur in soil and, under certain conditions, can be an effective management approach for residual hydrocarbons.
- Aging and weathering of anthropogenic hydrocarbons in soil can result in greater sequestering and less release and leachability of such chemicals.

Detailed knowledge on many of these and other important points is incorporated in the various chapters of this book. For the first time, relevant information about the composition of crude oils and condensates, about the technical basis for risk-based decisions for petroleum hydrocarbons, and about risk-based soil screening levels for specific chemicals such as petroleum hydrocarbons, polyaromatic hydrocarbons, volatile organic chemicals such as benzene, and metals have been brought together in one document. Equally relevant is the quality and integrated nature of the assembled information. Thus, this book provides scientific and field knowledge that are important for risk-based

decisions for the management of hydrocarbon-impacted soil at oil and gas industry exploration and production (E&P) sites.

The authors of the respective chapters are among the most knowledgeable in the nation in the respective scientific, technical, and policy areas. The authors are to be congratulated for having prepared a document that presents a large number of complex concepts and evaluations in a readable and succinct manner. This is an important and timely contribution that will have value to many parts of the environmental profession.

As indicated in Chapter 1, the general framework for risk-based decision-making was developed largely in response to sites impacted by hazardous materials. The framework has been refined over time and shown to be applicable to many sites and situations. This book provides information that can be used to apply the framework to oil and gas industry E&P sites. It should be noted, however, that the information in the book has much broader application. Specific information in the book has relevance, on a selected basis, to other sites that have petroleum hydrocarbons of the nature discussed. Such sites include Brownfield sites, some CERCLA and RCRA sites, and sites with contaminated sediments. Thus, a reader should consider the information provided for use not only at E&P sites, but also at other sites requiring possible remediation. It would do a disservice to the material in the book and to the insights provided by the authors if the information in the book were considered of relevance only to E&P sites.

Also noted in Chapter 1 is the fact that many other industrialized nations, such as Canada, New Zealand, and The Netherlands, use a risk-based approach for developing regulations and assessing individual sites. Australia, Great Britain, and Italy are among the other nations using or considering such an approach. However, the concepts involved and the RDBM approach are equally applicable to situations in developing countries. The knowledge that has been noted earlier indicates that: a) it is possible to allow some petroleum hydrocarbons to remain at a site and be protective of human health and the environment, and b) it is risk reduction that is the most desirable environmental goal, not achieving generic hydrocarbon concentration limits. The information in this book can be used by developing countries as they formulate environmental regulatory programs that are protective of human health and the environment. By doing so, developing countries can benefit from the comprehensive knowledge generated in the last decade. They thus will be at the leading edge of efforts to protect human health and the environment while at the same time meeting other social and economic needs.

As a final point, when considering the RDBM process, an important aspect is that of risk communication. The potential impact of chemicals at a site, knowledge of the uncertainties involved, the pathways of possible concern, and

analytical issues need to be discussed clearly and in a risk context. This book provides such information in a logical and understandable manner. As such, it is an important risk assessment and risk communication tool. It is my expectation that future evaluations of E&P sites, and of other relevant sites, will be much improved as a result of the information and logic presented in this book.

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List of Abbreviations

δ_{gw}	Groundwater mixing zone thickness
λ_s	Degradation constant in the saturated zone
λ_{unsat}	Degradation constant in the unsaturated zone beneath the contaminant source
λ_v	Volatilization rate constant for the contaminant source zone
ρ_b	Soil bulk density
ρ_s	Soil particle density
θ_a	Air filled porosity
θ_{as}	Volumetric air content
θ_o	Volumetric oil content in vadose zone soil
θ_{org}	Porosity filled with residual phase
θ_w	Water filled porosity
θ_{ws}	Volumetric water content
A	Cross-sectional area of the source
ADEC	Alaska Department of Environmental Conservation
ADL	Average dose level for an exposure pathway
Ag	Silver
API	American Petroleum Institute
As	Arsenic
ASTM	American Society for Testing and Materials
AT	Averaging time
Atm	Atmosphere
Ba	Barium
BCE	British Columbia Environment
Be	Beryllium
BTEX	Benzene, toluene, ethylbenzene, xylenes
BW	Body weight
C	Chemical concentration
Cal-EPA	State of California Environmental Protection Agency
CCME	Canadian Council of Ministers of the Environment
Cd	Cadmium

CERCLA	Comprehensive Environmental Response and Contingency Liability Act
CF	Calibration factor
C_o	Concentration in organic phase
COC	Chemical of concern
C_{of}	Final concentration of chemical in the oil phase
$C_{o\ max}$	Maximum concentration of chemical in the oil
C_{ppmv}	Concentration in vapor reported as parts per million volume
Cr	Chromium
CR	Contact rate
C_s	Concentration of chemical sorbed to soil
CSF	Oral cancer slope factor
CSM	Conceptual site model
C_T	Total concentration of chemical in soil
C_{TPH}	Total concentration of TPH in soil
C_v	Concentration of chemical in vapor phase
C_{vf}	Vapor concentration in soil outside of building structure or at ground surface
C_{vs}	Vapor concentration at the source of contamination
C_w	Concentration of chemical in water
$C_{w\ max}$	Maximum dissolved concentration
Cu	Copper
CVAAS	Cold-vapor atomic absorption spectrometry
D	Depth of source of contamination
DAF_{gw}	Dilution attenuation factor in groundwater
DAF_{mix}	Dilution attenuation factor in the groundwater mixing zone
DAF_o	Overall dilution attenuation factor
DAF_{sat}	Dilution attenuation factor in groundwater downstream of the contaminant source
DAF_{unsat}	Dilution attenuation factor in unsaturated zone
D_{air}	Molecular diffusion coefficient for chemical in air
D_{eff}	Effective diffusion coefficient in soil
D_{water}	Molecular diffusion coefficient for chemical in water

$D_{wT,S}$	Total effective diffusion coefficient
DRO	Diesel range organics
E&P	Exploration and Production
EC	Equivalent carbon
ED	Exposure duration
EF	Exposure frequency
EPC	Electronic pressure control
FAAS	Flame atomic absorption spectrometry
FID	Flame-ionizing detector
F_{oc}	Fraction of organic carbon in soil
F_{oil}	Fraction of oil in soil
FT	Fate and transport
GC	Gas chromatograph or gas chromatography
GFAAS	Graphite furnace atomic absorption spectrometry
GRO	Gasoline range organics
GW	Groundwater
$^{GW}GW_{ing}$	Protective concentration limit for ingestion of groundwater
H	Henry's Law constant or distance from bottom of contaminant source zone to the water table
Hg	Mercury
HI	Hazard Index
HQ	Hazard Quotient
HMPW	High melting point wax
HSW	High sulfur wax
I	Infiltration rate
ICP-MS	Inductively coupled plasma-mass spectrometry
ID	Inner diameter
IR_{soil}	Soil ingestion rate
IR_w	Water ingestion rate
K	Partition coefficient
K_d	Soil/water partition coefficient
KD	Kuderna-Danish
K_H	Henry's Law coefficient

K_o	Oil-water partition coefficient
K_{oc}	Partition coefficient for soil organic carbon
K_{oil}	Partition coefficient for oil
K_{ow}	Octanol-water partition coefficient
K_s	Soil-water sorption coefficient
$K_{T,S}$	Overall soil-water partition coefficient for the contaminant source zone
$K_{T, unsat}$	Overall soil-water partition coefficient for the unsaturated zone
L	Length of source area parallel to groundwater flow direction, or volatilization distance
LA	Louisiana
LCS	Laboratory control samples
LDF	Lateral dilution factor
LF	Leaching factor
LF_{sw}	Leaching factor from soil to water
LOAEL	Lowest-observed-adverse-effect level
M	Soil-to-skin adherence factor
MADEP	Massachusetts Department of Environmental Protection
MCL	Maximum contaminant level
MDL	Method detection limit
MF	Modifying factor
mg/kg	Milligrams per kilogram
mg/L	Milligrams per liter
MGP	Manufactured gas plants
Mo	Molybdenum
mol	Mole
MS	Mass spectrometry, or matrix spike
MSD	Matrix spike duplicates
MSDS	Material safety data sheet
M_{org}	Mass of chemical in organic phase
M_s	Mass of chemical sorbed to soil
M_T	Total mass of chemical in soil
M_v	Mass of chemical in vapor phase
M_w	Mass of chemical dissolved in groundwater

mV	Millivolts
MW	Molecular weight
MW _i	Molecular weight of contaminant of interest
MW _o	Average molecular weight of oil
MW _{TPH}	Average molecular weight of TPH mixture
NA	Not available or not applicable
NAPL	Non-aqueous phase liquid
ND	Non-detect
Ni	Nickel
NOAEL	No-observed-adverse-effect level
NOW	Non-hazardous oilfield waste
O&G	Oil and grease
ORNL	Oak Ridge National Laboratory
OSHA	Occupational Safety and Health Administration
P	Pressure
PAH	Polyaromatic hydrocarbon
Pb	Lead
PCL	Protective concentration level
PERF	Petroleum Environmental Research Forum
PF	Partition factor
PHC	Petroleum hydrocarbon
ppb	Part per billion
ppm	Part per million
PQL	Practical quantitation limit
PRG	Preliminary Remediation Goal
Q	Contaminant mass flux
QC	Quality control
R	Correlation coefficient, universal gas constant, or retardation factor
RAF _d	Dermal relative absorption factor
RAF _o	Oral relative absorption factor
RBC	Risk-based concentration
RBCA	Risk-based corrective action

RBDM	Risk-based decision making
RBSL	Risk-based screening level
RBSL _{s,GW}	Risk-based screening level that is protective of groundwater
RCRA	Resource Conservation and Recovery Act
RES	Residual saturation
RfC	Reference concentration
RfD	Reference dose
RfD _o	Oral chronic reference dose
RIVM	Dutch National Institute of Public Health and the Environment
RPD	Relative percent difference
RSD	Relative standard deviation
RT	Retention time
S	Solubility
SA	Skin surface area
Sb	Antimony
SCC	Soil contamination concentration
Se	Selenium
S _{eff}	Effective solubility
SFo	Oral cancer slope factor
S _i	Solubility of the compound of interest
SIM	Selected ion monitoring
SJV	San Joaquin Valley
Sn	Tin
SOC	Soil organic content
SPE	Society of Petroleum Engineers
SQG	Soil quality guidelines
SRM	Standard reference materials
SSL	Soil screening level
SSTL	Site-specific target level
T	Temperature
THQ	Target hazard quotient
TNRCC	Texas Natural Resource Conservation Commission
TOC	Total organic carbon

TPH	Total petroleum hydrocarbons
TPHCWG	Total Petroleum Hydrocarbon Criteria Working Group
TR	Target excess individual lifetime cancer risk
TRRP	Texas Risk Reduction Program
TX	Texas
U	Infiltration rate
UCM	Unresolved complex mixture
UF	Uncertainty factor
U_{gw}	Groundwater Darcy velocity
USEPA	United States Environmental Protection Agency
USGS	United States Geological Survey
UST	Underground storage tank
V	Vanadium
v	Seepage velocity
VF	Volatilization factor
VF_p	Ambient air partition factor for particulates
VF_{ss}	Ambient air partition factor for vapors
VP	Vapor pressure
W	Weight fraction
X	Mole fraction
X_{max}	Maximum mole fraction

Executive Summary

This book presents the scientific background material necessary to support a risk-based decision-making (RBDM) approach for managing hydrocarbon-impacted soil at oil and natural gas industry exploration and production (E&P) sites. Much of the information presented in the various chapters was generated as part of a multi-year joint industry Petroleum Environmental Research Forum (PERF) project that focused on improving the technical basis for environmental management of E&P sites. The general RBDM approach is largely based on guidance originally developed by the United States Environmental Protection Agency (USEPA). That framework was later refined by the American Society for Testing and Materials (ASTM) for evaluating individual chemicals and the Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG) and PERF for complex petroleum hydrocarbon mixtures. The information and approach described in this report have recently been used in the development of risk-based regulatory programs in several oil and natural gas producing states in the United States.

Detailed information about the composition of crude oils and gas condensates is summarized and the total petroleum hydrocarbon (TPH) fractions and individual chemicals of potential concern in these mixtures are identified. The fate, transport, and toxicity information necessary for estimating potential risks to human health is then described and used to generate risk-based screening levels (RBSLs) that can be used in a Tier 1, or screening level, risk evaluation. These RBSLs represent soil concentrations that are protective of human health and are calculated using exposure equations recognized by USEPA as providing conservative estimates (i.e., lower than necessary for the protection of human health) of acceptable concentrations in soil. The calculated Tier 1 RBSLs can be compared to regulatory criteria to determine whether the criteria are protective of human health, or in instances where there are no regulatory criteria, the RBSLs can be used as limiting concentrations for TPH or specific chemicals of concern in soil.

TPH RBSLs for Complex Mixtures of Petroleum Hydrocarbons

Tier 1 TPH RBSLs are determined for seventy crude oils that are representative of the wide range of crude oil types produced around the world. TPH RBSLs are also derived for fourteen gas condensates. These RBSLs are based on the potential non-cancer health risks that these mixtures might pose and typical exposure pathways that exist at E&P sites. The potential cancer risks are addressed in a separate chemical-specific analysis. The primary focus is on commercial and non-residential uses of the sites, which best represent reasonably expected land uses for E&P sites. Based on these land uses, the

exposure pathways of greatest concern are associated with direct human contact with hydrocarbon-impacted soil (i.e., soil ingestion, inhalation of soil particles, and dermal contact). Leaching to groundwater and volatilization to outdoor air are of lower concern for the complex mixtures as a whole.

The TPH RBSLs calculated for direct contact with soil impacted by this wide variety of crude oils range from 35,000 to 67,000 mg/kg (3.5-6.7% by weight) TPH for non-residential sites. TPH RBSLs for condensates range from 39,000 to 116,000 mg/kg (3.9-11.6% by weight) TPH. These values are significantly greater than the TPH concentration of 10,000 mg/kg that has often been used as the regulatory criterion for E&P sites. The TPH RBSLs for selected E&P wastes are also determined for the same exposure scenario. These values were very similar to those for the crude oils, ranging from 50,000 to 89,000 mg/kg (5.0-8.9% by weight). Since these results represent RBSLs for all of the types of oils produced around the world and because they have been shown to be conservative for associated wastes and soil, they can be used to set TPH RBSLs for crude oil and condensates present in soils at all E&P sites.

It is important to remember that these RBSLs apply to non-residential land use conditions. If a particular site is expected to be used for residential purposes, TPH RBSLs appropriate for that land use should be developed. Residential RBSLs may be an order of magnitude or more lower than those appropriate for non-residential land use.

Potential Health Risks of Metals, Polyaromatic Hydrocarbons, and Benzene

In addition to the potential risks posed by the petroleum mixture as a whole, which are addressed in terms of TPH, the potential risks posed by typical indicator chemicals are also considered. The concentrations of metals in crude oils are not sufficiently high to pose a significant health risk at residential sites even at an overall oil concentration in excess of 650,000 mg/kg (65 wt %). Therefore, metals are unlikely to be a major risk management consideration at crude oil spill sites, and routine analyses for metals in soils at crude oil spill sites is not recommended. However, it may be necessary to evaluate metals at those sites where multiple spills may have occurred or at landfarms which have received multiple applications of oily wastes.

The concentrations of polyaromatic hydrocarbons (PAHs) in crude oils and condensates are not sufficiently high to pose a significant health risk for residential land use, even at an overall oil concentration in excess of 14,000 mg/kg or (1.4 wt %). The only exception is naphthalene, a non-carcinogenic PAH, which may pose a risk at lower concentrations. The concern relates to naphthalene's potential for leaching to groundwater. Overall, these results suggest that carcinogenic PAHs are unlikely to be a major risk management

consideration at crude oil or condensate spill sites. Routine analysis for these chemicals in soil at E&P sites is not necessary to ensure protection of human health.

The understanding of the impact of benzene on the management of E&P sites is continuing to evolve. Benzene is typically considered to be a chemical of potential concern at gasoline release sites; however, most upstream regulatory programs do not routinely require benzene analysis of E&P site soils and do not routinely set regulatory limits for benzene in soil. In this study, benzene was detected in crude oils at a mean concentration of 1340 mg/kg oil and in condensates at a mean concentration of 10,300 mg/kg. However, some crude oils contain little or no benzene. The potential for benzene to leach to groundwater should be carefully evaluated at E&P sites where groundwater protection is an important consideration and where the oil or condensate is known to contain significant amounts of benzene. It may be appropriate to directly analyze for benzene at the site (using USEPA 8260) and to derive chemical-specific benzene RBSLs for groundwater protection. In deriving appropriate benzene RBSLs, careful consideration should be given to relevant environmental fate and transport processes, including volatilization and biodegradation. It is now known that assumptions made in previous screening level evaluations are overly conservative for benzene, because of its specific fate and transport properties. Previously published benzene RBSLs using these overly conservative assumptions may be 10 to 1000 times lower than necessary to protect human health.

Chemicals of Concern for E&P Site Management

TPH has historically been the primary criterion for environmental management at E&P sites. Although typical TPH regulatory limits used in the past have not been health risk-based criteria, the work conducted to date demonstrates that acceptable health risk-based TPH levels can be developed and that acceptable criteria for non-residential sites are well above those historically used. This indicates that TPH can continue to be an important criterion for health risk-based E&P site management programs. Measurements of bulk TPH using conventional analytical methods can continue to be used to assess compliance at most, if not all, E&P sites.

For crude oil and condensate spill sites, metals and PAHs are unlikely to exceed health risk-based levels. Volatile aromatics such as benzene, toluene, ethylbenzene, xylenes, and naphthalene may need to be evaluated on a site by site basis.

RBSLs for International Applications

The RBDM process is a scientifically defensible, flexible, and yet standard process that can be used to develop RBSLs. The health risk-based concepts have been developed in North America and Europe, but they are equally applicable to sites anywhere in the world. The RBSLs derived in this book are generally based on exposure pathways and assumptions commonly applied in the United States. Meaningful RBSLs for international locations can be developed if adequate consideration is given to relevant exposure factors for the new locations such as differences in lifestyle, climate, and local geology.

An Overview of Risk-Based Decision-Making for Site Management

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² ThermoRetec Consulting Corporation

Introduction

Risk-based decision-making is the process of making environmental management decisions based upon an assessment of the potential risks that chemicals at a site may pose to human health and the environment. The United States Environmental Protection Agency (USEPA) has developed a general framework for risk-based decision making based upon human health considerations, and has established general guidelines for determining what constitutes acceptable risk to human health [1,2]. These guidelines can be used to determine when some type of risk management action is required at a site. Although the overall framework for risk-based decision-making was originally developed for use at sites impacted by hazardous materials, in reality it is equally applicable to all types of sites, including oil and gas industry exploration and production (E&P) sites.

The general framework for risk-based decision-making was originally developed by the USEPA largely in response to the requirements of the Comprehensive Environmental Response and Contingency Liability Act of 1980 (CERCLA). This framework has been refined over time and several tiered approaches to risk-based decision-making have subsequently been developed. A major goal of the framework is to make certain that management decisions for environmentally impacted sites provide an adequate level of protection for human health and the environment. Therefore, a health risk evaluation process was developed and the overall risk characterization is used to guide site management decisions.

Risk-Based Decision-Making at Environmentally-Impacted Sites

Historically, regulatory programs in the United States have established environmental management goals (i.e., cleanup levels) for chemicals of potential concern at specific sites based on:

- Background (or naturally occurring) chemical concentrations (for example, those typically found in unaffected areas).

- Analytical detection limits.
- Concentrations that may be attainable if the most aggressive technologies were used for site remediation.

However, since none of these goals is directly tied to the actual risks posed by the chemicals of concern, there is no way to determine whether or not these goals actually protect human health and the environment. In addition, there is no way to determine the cost/benefit associated with achieving the management goals listed above, since the benefit of the action cannot be determined. Without any knowledge of the benefit resulting from a given action, there is no way to prioritize actions to focus them on those problems where the greatest potential for risk reduction exists. This could conceivably result in a portion of the public being left at risk, and in the misallocation of both technical and financial resources.

In contrast, risk-based approaches to site management clearly describe the potential health benefits that might result from a particular environmental management decision. Consequently, the actions that are taken at a site can be evaluated and prioritized based on the actual reduction in risk that would be achieved, and technical and financial resources can be allocated appropriately.

Like all technical methodologies and protocols, risk-based decision-making is not necessarily applicable to every situation at every site. For example, there may be instances where a risk-based assessment concludes that total petroleum hydrocarbon (TPH) concentrations at a specific site do not pose a health risk. However, these same concentrations may produce unsightly conditions that are not aesthetically acceptable for the current and/or future land use. In these instances, common sense should be used to guide site management decisions.

It is also important to think carefully about the assumptions that are made when using risk-based decision-making for site management. Since there tends to be limited data available to conduct a risk-based evaluation of a site, there is generally a need to make some basic assumptions during the risk evaluation. Examples of assumptions that need to be made may include the toxicity of the materials in question or the duration and extent of potential exposures. In every risk evaluation, it is important to understand the sensitivity of the risk-based decisions to the assumptions made in order to determine how robust the evaluation is and the circumstances that might justify the use of different assumptions. The greatest criticism of risk-based decision-making in site management is that it can be manipulated to produce any result that is desired by the user. The primary defense to this criticism is to make certain that all assumptions are technically justifiable, and to examine the sensitivity of the outcome to the more critical of these assumptions.

The Risk Evaluation Process

The risk evaluation process, as developed by the USEPA [2], involves four elements:

- Hazard Identification
- Exposure Assessment
- Toxicity (or Dose-Response) Assessment
- Risk Characterization

Simply stated, a quantitative risk evaluation involves identifying the chemicals of potential concern at a site, simulating their release and movement in the environment, estimating their uptake by both human and environmental receptors (a receptor is an exposed person, animal, or plant), and predicting the potential health effects of the exposure. Each of the technical elements of the risk evaluation process is described below.

Hazard Identification

Hazard identification is accomplished by collecting and reviewing site assessment data and identifying the chemicals of potential concern and the environmental media (e.g., soil, groundwater, and air) in which they can be found. It answers the question “What are the potential hazards at the site?”

Exposure Assessment

The exposure assessment answers the question “To how much of the chemicals of potential concern are receptors exposed?” The exposure assessment is an extremely important part of the risk evaluation process because it introduces site-specific factors into the characterization of the site risk. The exposure assessment can be thought of as a three-step process in which: (1) the site setting, which depicts the relative locations of the hazards and potential receptors, is characterized, (2) complete exposure pathways are identified, and (3) the magnitude of the potential exposure is estimated.

Characterizing the site setting identifies the receptors that might be exposed to the chemicals of potential concern. A key issue in identifying these receptors is the current and reasonably expected future land use for the site. Historically, regulatory agencies have required site managers to consider all potential future land uses, including residential use, in all risk analyses. This is not a reasonable assumption for most E&P sites where more realistic future land uses include ranch land, agricultural land, or park land. More recently, regulatory agencies in the United States have focused on protecting current land uses and have allowed more flexibility in the selection of appropriate future land use scenarios. This has resulted in more flexibility in developing regulatory criteria for site cleanup.

Once the receptors have been identified, the next step is to determine how they might be exposed. This is a process in which potentially complete exposure pathways are identified. In identifying these complete exposure pathways, the sources of the chemicals at the site are determined and the ways in which they may move around in the environment and be transported to places at which receptors might be exposed are considered. For example, if a crude oil is spilled on soil at a site, a worker in the area may be exposed by direct skin contact with the impacted soil. In addition, some of the components of the crude oil may volatilize into air and be inhaled by the worker, or some components may migrate through the soil into the groundwater, be transported to a drinking water well at some distance from the site, and subsequently be ingested. The final step of the exposure assessment is to quantify the potential exposure to receptors using standardized intake equations.

Toxicity (Dose-Response) Assessment

The toxicity assessment answers the question “What dose levels of the chemicals of potential concern may produce adverse health effects in people or other receptors?” In the toxicity assessment, chemicals are usually evaluated separately for their abilities to cause cancer and other adverse health effects. All chemicals have the inherent ability to cause adverse health effects at some dose level, but only certain chemicals have the ability to cause cancer. Most of the available toxicological data for both carcinogenic and non-carcinogenic chemicals have been generated in the laboratory using pure chemicals that have been added to the food or water of rats or mice. One of the major challenges associated with the use of these data is in extrapolating the results for individual chemicals to situations in which mixtures of chemicals, such as crude oil, may be of concern. A second challenge is in extrapolating the laboratory results obtained in rodents treated with chemicals to situations in which people are exposed to chemicals. In both cases, the USEPA includes uncertainty factors into the analysis to make certain that the toxicity of the chemical or mixture of chemicals is not underestimated.

Risk Characterization

The final step of the risk evaluation for a site is one in which the results of the exposure assessment are combined with the toxicity assessment to quantify the potential risks to human health and the environment. The result is a conservative risk estimate that is likely to overestimate the true risks posed by the site. In reality, the true risk will most likely be much lower than the estimated risk.

Quantitative Human Health Risk Evaluation

As described above, the risk evaluation process is generally composed of four elements:

- Hazard Identification
- Exposure Assessment
- Toxicity (or Dose-Response) Assessment
- Risk Characterization

Most often, this process is quantitative in nature, the result of which is a numerical estimate of risk. The equations used to estimate risk are based on those originally developed by USEPA [2]. The calculations and the default assumptions that are commonly used in the equations are specifically designed/selected to provide a result that is protective of human health.

Exposure Assessment: Calculation of Contaminant Intake

The quantitative exposure estimate determines the amount of chemical that is taken in by a receptor for a given exposure route. The primary exposure routes for humans are ingestion of groundwater, inhalation of air, dermal contact with soil, and ingestion of soil. In all cases, the calculation of chemical intake requires knowledge of:

- The concentration of the chemical in the impacted medium, i.e., soil (mg/kg), air ($\mu\text{g}/\text{m}^3$), or water (mg/L).
- The amount of the impacted medium that is taken in by the receptor (i.e., liters of air or water or kilograms of soil).

The amount of the impacted medium that is taken in is determined by identifying an exposure event, specifying the quantity of the medium that is taken in per event, and specifying the frequency and duration of the event. The intake is then converted to a dose level by dividing it by the body weight of the receptor and averaging over an appropriate time period. This yields an average daily dose or average lifetime daily dose expressed in mg/kg per day. The averaging time period depends upon the health effect that is being addressed. For example, the averaging time for carcinogenic effects is a lifetime of 70 years. On the other hand, for non-carcinogenic effects, the averaging time is equal to the duration of the exposure (e.g., 25 years for an adult worker).

Chemical intake for an exposure pathway is determined using the following equation:

$$ADL = \frac{C \times CR}{BW} \times \frac{EF \times ED}{AT}$$

where:

ADL = Average dose level (mg/kg BW-day)

C = Chemical concentration (e.g., mg/kg-soil or mg/L-water)

CR = Contact rate or the amount of impacted medium contacted per event (e.g., liters/day, kg/day)

EF = Exposure frequency (days/year)

ED = Exposure duration (years)

BW = Body weight of the receptor (kg)

AT = Averaging time of the exposure (days)

Derivation of Toxicological Dose-Response Factors

In estimating risk, the exposure estimate is combined with a toxicological dose-response factor. The dose-response factor depends upon the chemical, the route of exposure, and the health effect that is of concern (i.e., carcinogenic or non-carcinogenic). It is generally derived by USEPA [13], or other regulatory agencies, and is made available to the public for use by risk assessors. The data on which these factors are based are usually generated in laboratory studies using animals. The dose-response factors derived from these data include reference doses (RfDs) or inhalation reference concentrations (RfCs) for evaluating non-carcinogenic effects and cancer slope factors for evaluating carcinogenic effects as described below:

- **Reference Doses (RfDs — mg/kg-day):** Estimate of daily exposure that is likely to be without an appreciable risk of adverse (non-carcinogenic) health effects during a lifetime of exposure.
- **Reference Concentrations (RfCs — mg/m³):** Estimate of a continuous inhalation exposure to the human population that is likely to be without an appreciable risk of adverse (non-carcinogenic) health effects during a lifetime.
- **Oral Cancer Slope Factor [CSF — (mg/kg/day)⁻¹]:** Slope of the relationship between the oral dose received by a receptor and the carcinogenic response.

Calculation of Risk

The risk calculations for non-carcinogenic health effects are expressed in terms of a unitless hazard quotient that is calculated using the following equation:

$$\text{Hazard Quotient} = \frac{\text{Average Daily Dose (mg/kg - day)}}{\text{Reference Dose (mg/kg - day)}}$$

The threshold level of acceptability for the Hazard Quotient that has been established by the USEPA [1] is the value 1.0, although some state regulatory agencies within the United States have established different levels of acceptability. Hazard quotients greater than 1.0 typically require further site analysis or some sort of site action.

The risk calculation for carcinogenic health effects is based on a somewhat similar equation:

$$\text{Risk} = \text{Average Lifetime Daily Dose (mg/kg-day)} \times \text{Slope Factor (mg/kg-day)}^{-1}$$

This risk calculation also yields a unitless value. The acceptable individual excess lifetime cancer risk range established by the USEPA [1] is 10^{-4} to 10^{-6} (one-in-ten thousand to one-in-one million excess cancer risk). Many state regulatory agencies within the United States have established acceptable risk target levels within this range.

Tiered Risk-Based Decision-Making Frameworks

One drawback of the risk-based decision-making process, as originally developed by the USEPA, is that it can require a substantial investment of technical and financial resources, as well as time. Also, the data required to complete the risk evaluation are often not readily available. For these reasons, tiered strategies tailored for specific types of sites have recently been developed by United States regulatory agencies and by independent organizations to permit its cost-effective use. One example of a tiered risk-based decision-making framework is that developed by the American Society for Testing and Materials (ASTM).

The first significant development by ASTM was the *Standard Guide for Risk-Based Corrective Action Applied at Petroleum Release Sites* [3]. The development of this guide was driven by the need to cost-effectively and expeditiously manage underground storage tank (UST) sites. The guide was finalized in 1995 and it has since been recognized by the USEPA and used by many regulatory agencies in the United States to revise UST regulations. ASTM completed a second guide in April 2000 with the development of the *Standard Guide for Risk-Based Corrective Action* [4]. This effort expanded the previous guide by facilitating the use of risk-based corrective action in United States regulatory programs including voluntary cleanup programs, Brownfields redevelopment, CERCLA, and Resource Conservation and Recovery Act (RCRA) corrective action.

In addition to these national efforts by ASTM, several state environmental regulatory agencies within the United States have also initiated unified risk-based corrective action programs that include voluntary, CERCLA, and RCRA corrective action programs. Examples of these programs are the Massachusetts Contingency Plan [5], the Illinois Environmental Protection Agency Tiered Approach to Corrective Action Objectives [6], Louisiana Department of Environmental Quality Risk Evaluation/Corrective Action Program [7], and the Texas Natural Resource Conservation Commission (TNRCC) Risk Reduction Program [8].

Tier 1

Figure 1 illustrates the tiered risk-based decision-making approach described by ASTM, which is commonly referred to as the Risk-Based Corrective Action (RBCA) process [3]. In the first tier of the RBCA process, chemical concentrations in soil may be compared to generic “Tier 1” risk-based screening levels (RBSLs). RBSLs are chemical-specific concentrations in environmental media that are considered protective of human health. These screening levels are often derived by state or federal regulatory agencies using very conservative exposure assumptions. The USEPA has developed Tier 1 Soil Screening Levels (SSLs) [9], Preliminary Remediation Goals (PRGs) [10], Risk-Based Concentrations (RBCs) [11], and Human Health Medium-Specific Screening Levels [12] for evaluating potential human health effects at CERCLA sites. These screening levels are similar to RBSLs in that they are risk-based concentrations derived from standardized equations combining exposure information assumptions with USEPA toxicity data.

RISK-BASED CORRECTIVE ACTION PROCESS

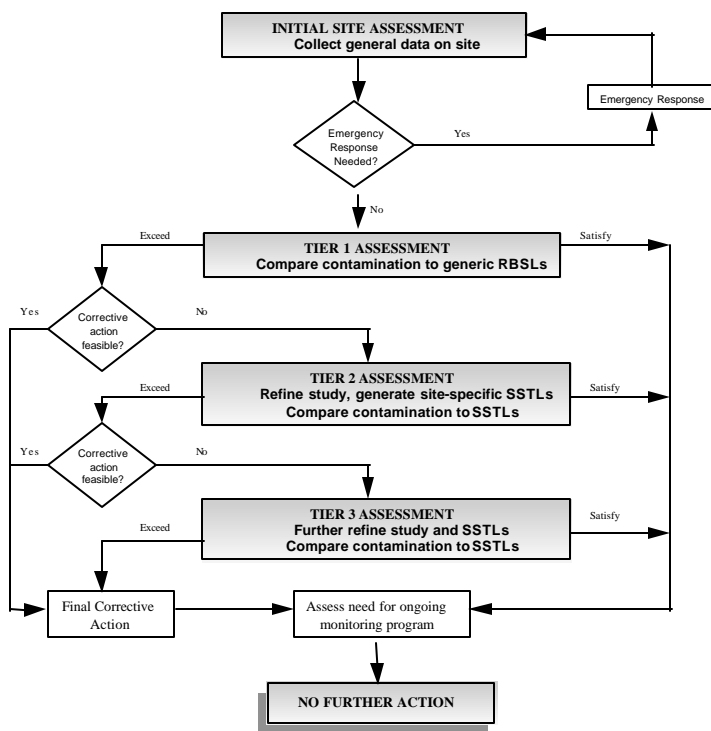


Figure 1. A RBCA flowchart illustrating tiers and decision points.

In addition to the screening levels developed by USEPA, some state programs have developed Tier 1 RBSLs. For example, the TNRC has developed Protective Concentration Levels (PCLs) as Tier 1 RBSLs [8]. A PCL is defined as the concentration of a chemical of concern which can remain within the source medium and not result in levels which exceed the applicable human health risk-based exposure limit or ecological protective concentration level at the point of exposure for that exposure pathway [8].

As shown in Figure 1, tiered approaches generally start with an initial screening stage, Tier 1, that uses a basic set of site assessment data and involves a comparison of the concentrations of chemicals in the different environmental media to predetermined Tier 1 RBSLs. If site concentrations are below the Tier 1 RBSL, the conclusion is drawn that chemicals of potential concern do not

pose a significant risk to human health or the environment and that no remedial action is necessary. If site concentrations exceed Tier 1 levels, the site manager generally has the option of remediating the site to Tier 1 levels or, alternatively, progressing to a more data and labor intensive Tier 2 or even Tier 3 analysis.

Tiers 2 and 3

Tier 2 and Tier 3 analyses generally require increasingly sophisticated levels of data collection and analysis, which in turn result in increased costs. The trade-off for these increased costs will generally lie in lower remediation and overall project costs, because the cleanup goals defined by a Tier 2 or 3 analysis are likely to be higher than Tier 1 levels, and thus less costly to achieve. The cleanup goals of the Tier 2 and 3 analyses are generally higher than the Tier 1 analysis because the generic assumptions used in the Tier 1 levels are replaced with more relevant site-specific assumptions and data. They are not higher because they are less protective of human health or the environment. In fact, all three tiers of risk analysis provide an equal level of health protection. Tier 2 and 3 risk-based concentrations are often referred to as Site-Specific Target Levels (SSTLs). ASTM [3,4] defines an SSTL as a risk-based remedial action target level for chemical(s) of concern developed for a particular site under the Tier 2 and Tier 3 evaluations.

Upon completion of each tier, the site manager reviews the results and recommendations, and decides if the cost of conducting the additional site-specific analyses is warranted. Using the tiered approach, an E&P site manager has the flexibility to forego the detailed risk characterization effort of a site-specific Tier 2 or 3 analysis and proceed directly to site actions that generally involve meeting conservatively low, generic site cleanup goals. In some cases, this approach may be the more cost-effective and more prudent site management decision.

Implementation of a Tiered Risk Approach

The development of tiered approaches for the risk-based analysis of sites was based on the premise that there are situations where conducting a detailed risk analysis may require more effort and time than immediate implementation of site remedial actions. For this reason, after every tier of risk analysis, the site manager must perform a cost/benefit evaluation to determine if it makes sense to proceed to the next level of risk analysis. Only if a clear benefit exists would the decision to move forward be made. For example, because the Tier 1 assessment is often based upon conservatively low, generic site cleanup goals, the extent of a site remedial action may be larger (and more expensive) than might be required if a more detailed site-specific Tier 2 analysis were conducted. However, additional time and expense will be incurred to complete the Tier 2 analysis. At this point the site manager must evaluate the potential reduction in site remedial costs that may be realized by conducting the Tier 2

analysis and compare that reduction to the additional cost of conducting the risk analysis. If the potential savings outweigh the potential cost, it would be in the manager's best interest to move forward with the Tier 2 analysis. In some cases, it is not the cost that drives the decision, but the schedule. If the time required to conduct the next tier of risk analysis is not acceptable to regulatory agencies or the public, then the decision to proceed with site remediation is essentially made.

The decision to use the tiered risk-based strategies for site management is usually dictated by the nature of the site contamination and the complexity of the site conditions. However, it may also be dictated by the governing regulatory agency, which may or may not accept the use of a tiered approach. At most E&P sites, it is likely that a tiered risk-based decision-making strategy will be the approach of choice. This is because E&P sites generally involve a known and very limited number of chemicals of potential concern (e.g., crude oil, gas condensates, and selected additives), and they have relatively small and simple operational footprints. Consequently, the lower tiers of risk analysis will often provide the most cost-effective site management approach.

Role of Generic Site Cleanup Criteria in the Risk-Based Decision-Making Process

As described in Chapter 2, most regulatory programs, including those with jurisdiction over E&P sites, have historically incorporated cleanup criteria that are not explicitly health risk-based levels. Instead, generic criteria have often been used, such as the commonly applied 1% TPH management level. For practical purposes, these generic criteria may be used as Tier 1 screening level criteria in a pseudo risk-based decision-making process. However, it should be recognized that those generic criteria that are not risk-based may or may not be protective of human health and the environment. One of the goals of a recent joint-industry research project sponsored by the Petroleum Environmental Research Forum was to derive generic risk-based screening criteria for E&P sites that could be compared to existing, non risk-based criteria currently used for E&P site management. See Chapter 8 for more information on RBSLs for TPH.

The Derivation and Use of Risk-Based Screening Levels

RBSLs (chemical-specific concentrations in environmental media that are considered protective of human health) can be derived from the risk equations by specifying an acceptable target risk level. The equations are then rearranged to determine the chemical concentration in the environmental medium of concern that represents this risk level.

The tiered risk-based decision-making approach developed by ASTM relies more on the use of RBSLs for site management decision-making, rather than on

an explicit calculation of site risk, as generally used in the classical approach by USEPA. The equation below is based on information provided by ASTM [3], and is used to calculate RBSLs for non-carcinogenic health effects for the exposure pathways of soil ingestion and dermal contact with soil:

$$\text{RBSL}_{ss} \left[\frac{\text{mg}}{\text{kg/Soil}} \right] = \frac{\text{THQ} \times \text{BW} \times \text{AT}_n \times 365 \frac{\text{days}}{\text{year}}}{\text{EF} \times \text{ED} \left[\frac{10^{-6} \frac{\text{kg}}{\text{mg}} \times (\text{IR}_{\text{soil}} \times \text{RAF}_o + \text{SA} \times \text{M} \times \text{RAF}_d)}{\text{RfD}_o} \right]}$$

where:

THQ = Target hazard quotient for individual constituents (unitless)

BW = Body weight (kg)

AT_n = Averaging time for non-carcinogens (years)

EF = Exposure frequency (days/year)

ED = Exposure duration (years)

IR_{soil} = Soil ingestion rate (mg/day)

RfD_o = Oral chronic reference dose (mg/kg-day)

RAF_d = Dermal relative absorption factor (unitless)

RAF_o = Oral relative absorption factor (unitless)

SA = Skin surface area (cm²/day)

M = Soil-to-skin adherence factor (mg/cm²)

Similar RBSL equations for other exposure pathways (i.e., inhalation of volatiles and particulates, ingestion of groundwater, and inhalation of vapor) are provided in the appendices of the ASTM guides [3,4]. It should be noted that the derivation of RBSL equations that are appropriate for use with complex mixtures, such as crude oil, requires additional manipulations of the equations used above.

There are several factors in the risk equations that address the availability of soil-bound contaminants to the human receptor. These are the dermal relative absorption factor, or RAF_d, the oral relative absorption factor, RAF_o, and the ambient air partition factors for both particulates (VF_p) and vapors (VF_{ss}). These factors are included because the soil tends to bind many of the contaminants and prevent them from coming into contact with the receptor and causing an impact. This matrix effect is caused by the soil, is recognized by the USEPA, and is currently the subject of a great deal of research by universities, industry consortia, and the USEPA.

For the vapor and groundwater exposure pathways, the acceptable contaminant concentrations in the air and groundwater can be used to back-calculate a

contaminant concentration in soil that will be protective of these other media. In other words, a contaminant concentration in soil can be determined that will not result in an exceedance of the acceptable contaminant concentrations in air or groundwater. To complete these back-calculations, a volatilization factor (VF, $[\text{mg}/\text{m}^3]/[\text{mg}/\text{kg}]$) and leaching factor (LF, $[\text{mg}/\text{L}]/[\text{mg}/\text{kg}]$) are required. The former predicts the amount of contaminant that will partition between the soil and the vapor, while the latter predicts the partitioning from the soil to the aqueous phase [3].

Other parameters required for the calculation of RBSLs include body weight, exposure frequency, exposure duration, soil and water ingestion rates, air inhalation rates, averaging times for carcinogens and non-carcinogens, skin surface area, and soil-to-skin adherence factor. The USEPA has developed default values for each of these parameters that can be used if no other site- or chemical-specific data are available. Many state regulatory agencies within the United States have also made recommendations for their programs. Where appropriate, default values are available for several potential human receptors including workers, and adult and child residents.

RBSLs will not be the same for all routes of exposure. This is because the dose of a contaminant that a receptor receives depends upon the route of exposure and the concentration of the contaminant in the different environmental media. For this reason, it is possible to have several RBSLs for a contaminant at a given site (i.e., one RBSL for each exposure pathway). The management of the site requires that the lowest of these RBSLs be used to support the overall risk-based decisions that are made at the site. Considering the nature and composition of crude oils (i.e., low in volatile or water-soluble components that could partition into air or water), it is generally the RBSLs for direct contact with hydrocarbon-impacted surface soils that strongly influence E&P site management decisions. The receptors of concern are most often onsite workers or other non-residential receptors depending upon the anticipated future land use of the site.

International Risk Programs

Risk-based decision-making programs are not unique to the United States. For example, Canada, New Zealand, and the Netherlands have all adopted risk-based decision-making into their site management and cleanup programs. Many other countries are also considering developing their own risk-based decision-making programs. This is appropriate because the basic concepts of risk-based decision-making are equally applicable everywhere in the world. However, in practice, it is not a simple task. To develop a risk-based decision-making program that truly protects human health and the environment, it is necessary to collect information about how people or other receptors may be exposed to environmental chemicals in the particular country or region of concern. It is not

sufficient to merely assume that decisions made and/or Tier 1 RBSLs derived for programs developed in other parts of the world are appropriate for a new application in a new location. Country and/or region-specific information is necessary because living and working conditions in the Netherlands, Canada, or the United States may be quite different than in countries like Nigeria or Thailand. For example, some differences that may affect exposures include the length of time that people typically live in the same house, whether groundwater is consumed and how much is consumed, and how many days per year a worker spends at his job. The Dutch do not include exposure to groundwater in their risk program because their citizens do not drink groundwater. In the United States, consumption of groundwater is common and this pathway is an integral part of risk evaluation.

A brief summary of some of the international risk-based decision-making programs and Tier 1 RBSLs used in these programs is provided below.

Dutch National Institute of Public Health and the Environment (RIVM)

In 1994, the Dutch RIVM (National Institute of Public Health and the Environment) published soil and groundwater Target and Intervention Values [14]. Intervention Values for soil are defined as the concentrations above which soils are considered to be seriously contaminated, and are applicable to all sites exceeding 25 m³ in size. Target Values indicate the soil quality levels ultimately aimed for and are usually based on background chemical concentrations in soil in the Netherlands. In applying these values to individual sites, it is generally concluded that further site investigation is required if the soil concentration of a given chemical exceeds this criterion:

$$\frac{\text{Intervention Value} + \text{Target Value}}{2}$$

The target values are derived based on human health toxicity information for each chemical of concern and residential exposure estimates are derived using the Dutch CSOIL model. Several different residential exposure pathways are considered including ingestion of soil, ingestion of crops grown in impacted soil, and inhalation of indoor air. In selecting the overall exposure pathway of concern, RIVM derives “serious soil contamination concentrations” (SCCs) for each of the exposure pathways and then selects the most conservative (i.e., the lowest) concentration to propose as the overall Intervention Value for that chemical. A tiered risk approach is not used and commercial exposure scenarios are not considered in the Netherlands.

Canadian Council of Ministers of the Environment (CCME)

In 1991, CCME published *Interim Canadian Environmental Quality Criteria for Contaminated Sites* [15] and, in 1996, released a follow-up report, *A Protocol*

for the Derivation of Environmental and Human Health Soil Quality Guidelines [16], to derive Soil Quality Guidelines (SQGs) that will replace the 1991 criteria. The Canadian protocol considers potential exposures to both human and ecological receptors for given land uses. SQGs are derived based on exposure scenarios for agricultural, residential/parkland, commercial, and industrial land uses for jurisdictions in Canada. For each of the four land uses, CCME selects final generic SQGs for chemicals in soil based on the lowest value generated by either of the environmental or human health approaches. The protocol also identifies indirect routes of exposure including consumption of meat, milk, and produce from agriculture land, and consumption of homegrown produce from residential land.

In December 2000, the CCME published *Canada-Wide Standards for Petroleum Hydrocarbons (PHCs) in Soil: Scientific Rationale* [17] to address different types of hydrocarbon fractions. Following the approach described by the United States Total Petroleum Hydrocarbon Criteria Working Group [18], the CCME has defined four broad hydrocarbon fractions (F) including F1: C₆ to C₁₀; F2: >C₁₀ to C₁₆; F3: >C₁₆ to C₃₄; and F4: C₃₄+. Aliphatic and aromatic sub-fractions are handled separately. With respect to management of PHCs, additional factors considered in CCME's Tier 1 level include: ignition hazard, odor and appearance, effects on buried infrastructure, formation of non-aqueous phase liquids, and socioeconomics and technological capabilities.

New Zealand Ministry for the Environment

In 1999, New Zealand's Ministry for the Environment published *Guidelines for Assessing and Managing Petroleum Contaminated Sites in New Zealand* [19]. The Ministry presents a tiered risk-based approach to site assessment and development of soil and groundwater acceptance criteria for petroleum hydrocarbon contaminated sites. Tier 1 acceptance criteria are summarized in look-up tables and site-specific criteria used to develop Tier 2 and 3 criteria are outlined. Tier 1 acceptance criteria have been developed for a wide range of possible site characteristics rather than a single generic scenario. For example, the Tier 1 criteria include consideration of various land uses, such as agricultural, residential, commercial/industrial, and maintenance workers. Also considered are soil type (8 soil profiles are represented), depth of soil contamination, e.g., <1 meter, 1-4 meters, and >4 meters, and depth of groundwater from ground surface, such as 2-4 meters, 48 meters, and >8 meters. New Zealand specifies specific compounds of concern for each type of refined product for use in deriving Tier 1 soil acceptance criteria.

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Technical Basis for Current Soil Management Levels of Total Petroleum Hydrocarbons

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Introduction

This chapter reviews the technical basis for the 1% total petroleum hydrocarbon (TPH) management level for land management of exploration and production (E&P) wastes as recommended by the American Petroleum Institute (API) and provided in state regulations within the United States (e.g., Louisiana (LA) 29b and Texas (TX) Rule 91) and practice. The limitations of the 1% TPH management level are discussed and the need to develop risk-based management levels based on site-specific information is introduced.

Crude oil from a producing formation and diesel added to drilling mud are the chief sources of petroleum hydrocarbons in E&P wastes [1]. Gross analysis of petroleum hydrocarbons within a waste may be reported as oil and grease (O&G), TPH, or total organic carbon (TOC). O&G is determined by gravimetric analysis of a solvent extract, TPH is determined by infrared analysis of a solvent extract, and TOC is analyzed by wet oxidation of a sample. O&G was the predominant analytical method used to measure petroleum hydrocarbon content of E&P wastes prior to the 1990's, with TPH becoming the predominant analytical method since that time.

Initially, a 1% TPH concentration in soil was used as a guidance value for E&P wastes that were land-managed. The 1% TPH guidance value was developed based on two criteria: the first was the impact of hydrocarbons on plant life and the second was hydrocarbon mobility to groundwater. Over time, certain United States regulatory agencies adopted the 1% TPH guidance value as a regulatory limit for the hydrocarbon content of land-disposed E&P wastes. At sites where oily wastes having TPH concentrations greater than 1% have been land-disposed, the regulatory limit of 1% is sometimes used as a soil cleanup standard. In the paragraphs that follow, the terms "guidance value," "regulatory limit," and "cleanup standard" are used where appropriate; the term "management level" is used in instances where any of these terms may be appropriate.

Development of State E&P Waste Regulations Within the United States

Prior to the early 1980's, drilling wastes were handled in a manner that met the requirements of the landowner, that were protective of surface water, and that met aesthetic requirements. Closure of a site often consisted of drying and burying the waste materials, and contouring the land surface. The landowner was either paid for damages incurred to the land surface, or the area was reclaimed [2]. Major impacts to soils and crops were usually attributed to excess salts [3,4]. Effects of diesel oil on plants were considered less severe and of shorter duration than salt damage. During this time frame, regulations were primarily concerned with the quality of effluent reaching surface water. These water quality effluent requirements were generally met with conventional oil-water separators and other equipment [5]. In remote production areas, aesthetic requirements were met when the landowner was satisfied that the site was returned to a condition that was consistent with its original use.

In 1976, the Resource Conservation and Recovery Act (RCRA) was enacted to regulate solid waste and resource recovery in the United States for all but a few exempt wastes. The wastes that were (and still are) exempt include those associated with the exploration, development, and production of crude oil or natural gas [6]. The exemption broadly states that oil and gas wastes should not be regulated as hazardous waste, if they are being managed under existing regulatory programs in a way that adequately mitigates or prevents harm to the environment. Therefore, it has been up to state regulatory agencies to determine adequate management requirements for oilfield wastes, including oil-containing wastes.

The State of Louisiana was at the forefront of establishing regulations which specifically defined environmental standards for E&P wastes [7]. Early regulations required the protection of surface water from oilfield wastes, though oilfield wastes were not defined [8]. It was the Louisiana regulation of 1986 that clearly defined non-hazardous oilfield waste (NOW) and set forth regulatory requirements for O&G in soil, along with other components [9]. Landfarming of drilling pit contents required a final O&G content of the waste/soil mixture to be less than or equal to 1% dry weight; burial of the mixture onsite required a final O&G concentration of less than or equal to 3% dry weight [9].

A review of current upstream TPH regulations in North America (see Table 1) indicates that they are highly variable, ranging from 100 to 10,000 mg/kg soil. A few states (e.g., Texas, Colorado, Wyoming, and New Mexico) incorporate some broad risk concepts for determining appropriate TPH regulatory limits by evaluating site-specific conditions such as depth to groundwater and proximity to residential areas.

Table 1. Summary of TPH regulations for E&P sites in 1999 [10].

State/Province	TPH Regulatory Limit (mg/kg Soil)	Comments
Colorado	10,000 1,000	Non-Sensitive Sensitive
Louisiana	10,000	Land Treatment of NOW
Michigan	10,000	Was 250 mg/kg
New Mexico	100; 1,000; 5,000	Site Dependent
Texas	10,000	Railroad Commission Rule 91
Wyoming	1,000 to 10,000	Site-by-Site Basis
Alberta	1,000	

NOW = Non-Hazardous Oilfield Waste

The State of Colorado has established different TPH limits for sensitive sites (1,000 mg/kg) and non-sensitive sites (10,000 mg/kg). They define sensitive areas as those areas vulnerable to potential significant groundwater impacts and areas subject to concentrated human or wildlife use, such as parks, recreation sites, urban or suburban areas, and wildlife refuges [11,12]. New Mexico uses ranking criteria based on the general site characteristics “to determine their relative threat to human health, fresh waters and the environment.” The ranking criteria include depth to groundwater, distance from oil wellhead to water sources, and distance to surface water body [13].

Only one state, Michigan, has changed its TPH regulations for upstream sites based upon risk of crude oils to human health. In 1997, the Michigan Department of Environmental Quality changed the regulatory limit for TPH in soil at upstream sites from 250 mg/kg to 10,000 mg/kg based upon a risk evaluation of the crude oils produced in their state [14].

The Technical Basis for the 1% TPH Management Level

Petroleum Hydrocarbon Impact on Soils & Plants

A review of the literature that was used to develop API’s 1% TPH guidance level indicated that at “...1% or less of mixed hydrocarbon, little or no (plant) yield reduction is expected based on existing information [15].” Also, where the loading was between 1 and 5% petroleum hydrocarbon in soil, the site recovered after one growing season [15]. This recovery was the result of hydrocarbon “assimilation” by the soil, which is a combination of biodegradation, evaporative loss, and the binding of the petroleum hydrocarbons to soil organic matter.

There have been a number of explanations for petroleum hydrocarbon impacts on soil and plants. Early work made the distinction between acute and chronic plant injury, and biophysical and biochemical effects [16]. Petroleum hydrocarbons could exert a direct toxic effect by dissolving plant tissue. Poor growth was attributed to suffocation of the plants caused by the displacement of air in the soil pores by oil or the exhaustion of oxygen by increased microbial activity [16]. Also, there may be interference with plant-soil-water relationships, and toxicity from sulfides and excess available manganese produced during the biological decomposition of the hydrocarbons [17]. Damage to cell membranes, reduced transpiration rate, increase in respiration rate, and inhibited translocation were also implicated [18]. The severity of the effects noted depends upon the constituents and amount of oil, on the environmental conditions, and on the species of plant [18]. A distinction has also been made between rapid or acute injury caused by light oils, and slow or chronic injury resulting from heavy oils [19].

The following excerpts capture much of the essence of the early work in this field [20]:

- “The damage that oil does is due mostly to the prevention of the plant from obtaining sufficient moisture and air and from ramifying its roots: very little is due to toxicity, as such.”
- “Crude petroleum is converted to soil organic matter by bacteria and fungi.”
- “...the organic matter improves soil physical conditions.”

Thus, the development of the 1% TPH guidance level in soil was originally based on the issue of toxicity to plants. If the amount of petroleum hydrocarbon in soil is kept at or below this level, and there are acceptable salt and pH levels, there should not be significant reductions in plant yield, thus meeting landowner requirements.

More recent studies confirm the earlier studies on plant growth and germination for heavy or weathered crude oil. However, light or fresher crude oil may be found to require more stringent guidance. Chaineau et al. [21] found that the phytoavailability of complex mixtures of hydrocarbons that have low octanol-water partition coefficients (K_{ow}) is negligible, even when the soil petroleum hydrocarbon content is as high as 1%. Phytotoxicity was found to be greater for low molecular weight and aromatic hydrocarbons and varied greatly with hydrocarbon concentration in the soil and plant species [21]. Salanitro et al. [22] found a similar molecular weight relationship. Residual TPH in which germination was not affected (<4 to 27% reduction) in bioremediated soils (10 months treatment) varied from 7,000 to 10,000, from 8,200 to 8,600, and from

1,000 to 1,200 mg/kg for the heavy, medium, and light oily soils, respectively [22].

Current understanding of toxicity issues suggests that soil toxicity considerations may expand beyond plant toxicity alone. Other potential ecotoxicity issues are now being examined. For example, recent studies have examined earthworms [23] as well as other soil invertebrates [24].

Petroleum Hydrocarbon Impact on Groundwater Resources

If a sufficient quantity of hydrocarbon is released to a soil, the hydrocarbon will migrate through the soil as a non-aqueous phase liquid (NAPL). As the NAPL moves, some will remain in the pore spaces of the soil, until there is no longer sufficient volume of NAPL remaining for migration to occur. At this point, the NAPL in the soil is said to be at residual saturation. The 1% soil TPH guidance value was selected to be below the minimum level required for hydrocarbon mobility (or less than the residual saturation). Therefore, the guidance value of 1% TPH in soil prevents movement of NAPL toward groundwater receptors.

Researchers have confirmed that hydrocarbon migration is not a problem at low percentages of hydrocarbons in soil. Raymond et al. [25] found that by adding approximately 2% oil to the top 15 centimeters of soil, 99% remained within the top 20 centimeters after 1 year. When hydrocarbon loading rates of 3 to 13% per year were added, no significant oil migration was found below the zone of incorporation [25]. Brost and DeVaul [26] tried to determine a conservative NAPL concentration in unsaturated soil below which NAPL would be immobile. Unsaturated soil samples were saturated with hydrocarbons and then allowed to drain. The amount of residual hydrocarbon remaining in the soil pores was then quantified. Brost and DeVaul determined the residual saturation for middle distillates and fuel oils to range from 0.8 to 5.0% [26]. The variability is believed to be attributable to experimental method variability, variation in soil type, unique chemical properties and measurement differences.

When oil enters the soil as a NAPL there is natural separation of the hydrocarbon constituents due to exposure of the NAPL to the solid phase, vapor phase, and water phase within the soil. The higher molecular weight compounds are generally less mobile and stay near the source location, while the lighter weight compounds migrate deeper into the subsurface because of greater aqueous solubility [20]. Biodegradation of these compounds may play a role in preventing transport to groundwater. Webster and Loehr [27] studied the rate of hydrocarbon release for six soils containing petroleum hydrocarbons. Their work indicated soil hydrocarbons containing slightly to moderately weathered diesel range organics were more available for release when compared to weathered crude oil [27].

A mathematical model (called VADSAT) was developed by API to characterize the leaching of hydrocarbons from land-disposed wastes [28]. The VADSAT model was used to predict the fate and transport of selected organic components contained in E&P associated wastes. The model simulations considered various input scenarios that included: a) a variety of hydrogeological characteristics, b) four chemicals [benzene, toluene, ethylbenzene, and xylene (total)], c) six waste types, d) different disposal scenarios, e) infiltration and biodegradation, and f) 500 and 1,500 feet groundwater well receptor locations. The percent oil content varied with the different waste type. The waste management scenarios assumed average oil content from 1% for land spreading/burial to 2.5% for road spreading. There were 1,144 VADSAT computations for the various hydrogeological and waste scenarios described above. All VADSAT simulations resulted in groundwater concentrations at the receptor locations that were less than the United States Environmental Protection Agency (USEPA) groundwater Maximum Contaminant Levels (MCLs) for benzene, toluene, ethylbenzene, and xylene (total) in drinking water. Based on the available studies, the 1% TPH soil management level appears to be justifiable because it is protective of groundwater resources.

Impact of Biodegradation on Hydrocarbon Concentrations

Biodegradation of petroleum hydrocarbons has been well documented in the literature and bioremediation is recognized as a cost-effective method to treat soils and other E&P wastes containing petroleum hydrocarbons. In many situations, a 1% TPH management level is achievable through biodegradation. Biodegradation of petroleum hydrocarbons involves the metabolism of certain hydrocarbon compounds (alkanes, alkenes, aromatics, and polars) by indigenous soil microbes. The petroleum hydrocarbons are converted to carbon dioxide, water, and biomass. Many factors have been identified that affect both the kinetics and the extent of hydrocarbon biodegradation. These include soil properties such as pH, temperature, moisture, aeration, and nutrient status; as well as hydrocarbon characteristics.

Studies and reviews in the literature have documented the initial petroleum hydrocarbon loading rates in soil and the extent of soil hydrocarbon biodegradation. An industry review prepared for API in 1983 of land treatment practices indicated that 70 to 90% of oily sludge hydrocarbons that were applied to surface soils at loading rates of 1 to 5% were removed, primarily through biodegradation [29]. Loehr et al. [30] studied the treatability of an oily sludge in field plots in a silty loam soil and demonstrated that 60 to 70% of the initial oil and grease (2 to 5.5%) hydrocarbons were biodegraded within 2 to 3 years. Studies have demonstrated that degradative processes in soils attenuate the more mobile, light-end aromatic and water-soluble petroleum hydrocarbons, leaving behind the more recalcitrant hydrocarbons with little potential for contaminant migration. Huesemann and Moore [31] showed that 93% of the saturate and

79% of the aromatic hydrocarbon compounds having carbon numbers in the range of C_{10} - $C_{44}+$ were degraded in a sandy soil containing weathered Michigan crude oil (medium API gravity) with an initial concentration of 3% TPH. The study also indicated that the polar fraction was resistant to microbial metabolism and did not degrade during the 5.5-month long test.

Work by Huesemann [32] on the limits and extent of TPH remediation in different soils showed that 90% of the alkanes and monocyclic saturates and 50 to 70% of the aromatic compounds ($<C_{44}$) were degraded. Other research indicates that overall bioremediation effectiveness was dependent upon hydrocarbon types present and was not affected as much by soil type, nutrient addition, microbial populations, or treatment conditions [22]. Recently, a study of bioremediation showed that after bioremediation, petroleum hydrocarbons in oily soil decreased from 70 to 90%, from 40 to 60% and from 35 to 60% for those carbon number species in the range of C_{11} - C_{22} , C_{23} - C_{32} , and C_{35} - C_{44} , respectively [22]. In a pilot study designed to determine the fate of hydrocarbon constituents during land treatment of soil impacted with fresh Michigan crude oil (3.1 wt % TPH), results indicated that biodegradation was the primary pathway for TPH removal, accounting for 94% removed in 1 year [33].

The 1% TPH soil management level seems to be supported by both earlier and more recent investigations of petroleum hydrocarbon biodegradation. Cleanup standards that are less than 1%, while achievable in some situations, would be difficult to achieve at sites containing residual weathered petroleum hydrocarbons.

Summary

The 1% TPH management level used by Texas, Louisiana, and other regulators has been shown to be protective of groundwater resources and plant life. Also, the 1% TPH management level was shown to be achievable, specifically through bioremediation.

Although the 1% TPH management level may be adequate in many cases, risk-based cleanup standards are still needed to address the human health risks of particular hydrocarbon mixtures. The specific components of crude oil must be identified and the potential risks evaluated for those sites at which human exposures may be of concern. For this reason, within the last 10 years, technical methods have been developed to determine soil and groundwater corrective action cleanup criteria using a site-specific and human health risk-based approach. These methods are summarized in this book, and crude oil composition data are provided to aid in the risk evaluation. Risks to ecological receptors (other than plants) may also need to be considered, but the state of the science is not as advanced as that for human health risk assessment.

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Composition of Crude Oils and Gas Condensates

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Introduction

One of the basic principles of risk-based decision-making is that the decision-maker must have a good understanding of the composition of the material of concern. Therefore, knowledge of the chemical and physical characteristics of crude oils and condensates is required for the effective application of risk-based decision-making at exploration and production sites. A summary of the chemical and physical properties of both condensates and crude oils is presented in this chapter. Crude oils are defined as mixtures of hydrocarbons that exist in the liquid phase in underground reservoirs and that remain in the liquid phase at atmospheric pressure. Condensates are mixtures of hydrocarbons that are in the vapor phase under reservoir pressures and temperatures but become liquid under atmospheric conditions.

Molecular Structure of Hydrocarbons

Petroleum hydrocarbons are organic compounds comprised of carbon and hydrogen atoms arranged in varying structural configurations. In the broadest sense, petroleum hydrocarbons can be divided into two classes of chemicals, the saturates, which have only single bonds between carbon atoms, and the unsaturates, which have at least one double bond between carbon atoms (Figure 1). The saturates, also referred to as alkanes or paraffins, are comprised of three main subclasses of compounds based on the structure of their molecules, either straight chains, branched chains, or cyclic (see Figure 2). (The terms saturated and aliphatic hydrocarbons are interchangeable and both are used to describe this group of compounds.) Straight-chain compounds are known as normal alkanes (or n-alkanes). The branched-chain compounds are designated isoalkanes and the cyclic, or ring-like compounds, cycloalkanes. More familiar terms used by petroleum geologists to describe these structures are paraffins for alkanes and naphthenes for cycloparaffins or cycloalkanes.

Within the unsaturates, there are two main subclasses of compounds, aromatics and olefins. Aromatic hydrocarbons are comprised of one or more unsaturated cyclic structures, or rings. Benzene contains one such ring, while polycyclic

aromatic hydrocarbons (PAHs) contain two or more rings (e.g., phenanthrene has three unsaturated rings). Olefins contain double bonds between two or more carbon atoms. Olefins are not found in crude oil or condensates because they are readily reduced with hydrogen to paraffins in the reservoir [1]. Olefins are formed during refining of crude oils and they are present in most refined products. A classification of petroleum hydrocarbons by structure or molecular type is shown in Figures 1 and 2.

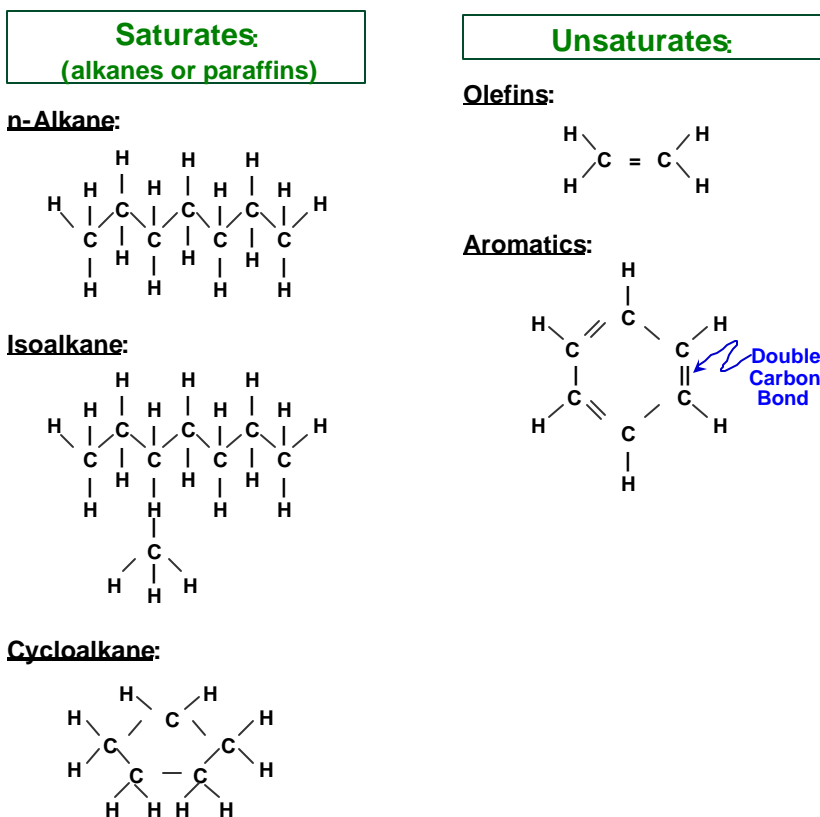


Figure 1. Examples of petroleum hydrocarbon structures .

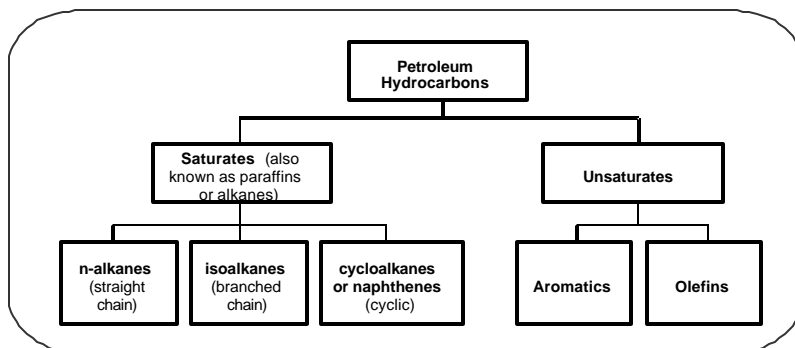


Figure 2. Chemical classification of petroleum hydrocarbons [2].

Crude Oil Composition

Crude oil is composed almost entirely of the elements hydrogen and carbon, in the ratio of approximately 1.85 (hydrogen):1 (carbon). In addition to the hydrocarbons, there are also two non-hydrocarbon fractions that contain elements in addition to carbon and hydrogen, such as nitrogen, sulfur, and oxygen. These elements constitute less than 1% to as much as 7% of some crude oils [1]. These non-hydrocarbon fractions are the asphaltenes and resins.

Hydrocarbons comprise the majority of the components in most crude oils and are the compounds that are primarily, but not always, measured as total petroleum hydrocarbons (TPH). The primary saturated and unsaturated hydrocarbons consist of n-alkanes, isoalkanes, cycloalkanes, and the mono-, di-, and tri-aromatics; there are no olefins in crude oil. Crude oils vary in appearance from straw yellow, green, and brown to dark brown or black in color [3].

Crude Oil Classification

Petroleum geologists often classify crude oils based on their hydrocarbon class composition. Several classification schemes have been published [4,5,6], including that shown in Figure 3. The composition of an example crude oil is presented in Table 1. This oil is a 35°API gravity oil that would be classified as a naphthenic oil.

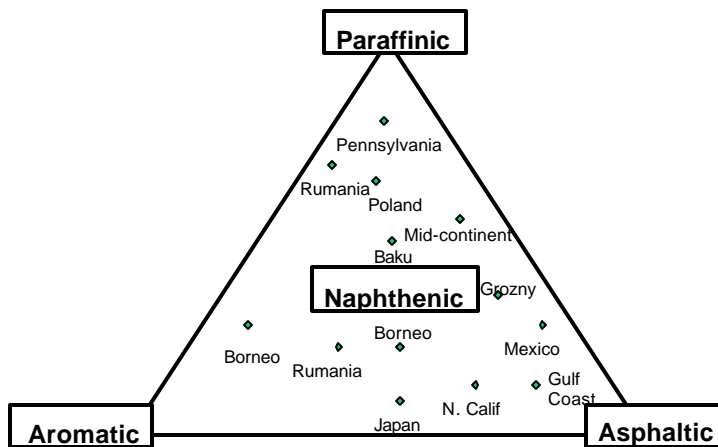


Figure 3. Classification of crude oils based on relative amounts of paraffins, naphthenes, asphaltenes, and aromatics [6].

Table 1. Composition of a naphthenic 35°API-gravity crude oil [1].

Molecular Type	Weight Percent
Paraffins	25
Naphthenes	50
Aromatics	17
Asphaltenes	8
Total	100

The composition of 636 crude oils from around the world have been compared by Tissot and Welte as shown in Figure 4 [7]. These data reveal that the proportions of saturates, aromatics, resins, and asphaltenes can vary dramatically among crude oils, with the majority of crude oils lying within a composition envelope that is bounded in the following manner:

- 40 to 80% Saturates
- 15 to 40% Aromatics
- 0 to 20% Resins and Asphaltenes

Tissot and Welte found that 95% of the crude oils produced around the world fell into this distribution pattern as shown in Figure 4.

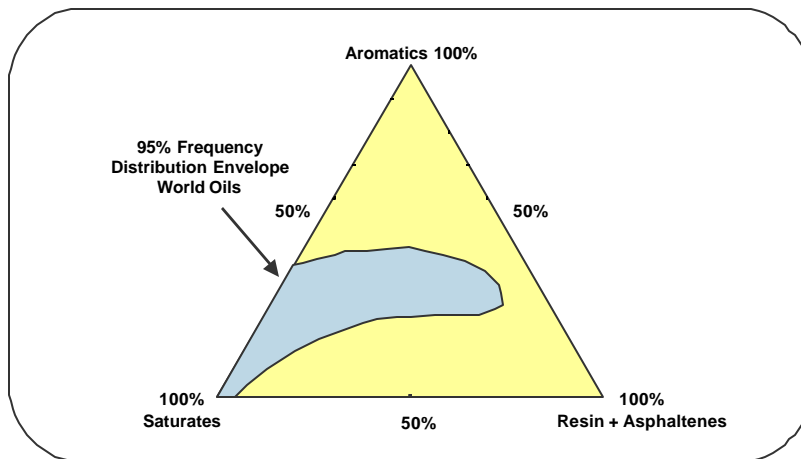


Figure 4. Ternary diagram showing the class composition of crude oils.

Carbon Number

It would be extremely difficult to identify all of the components of crude oils and fuels, so petroleum and petroleum products are characterized in terms of boiling range and approximate carbon number. Petroleum products can be classified by their distillation temperature, or boiling point ranges, which is also an indication of the carbon number range of each fuel. Figure 5 shows boiling points and carbon ranges for six common crude oil products [8]. The composition (in terms of refined petroleum products and carbon ranges) of a 35°API-gravity oil is shown in Table 3 [1].

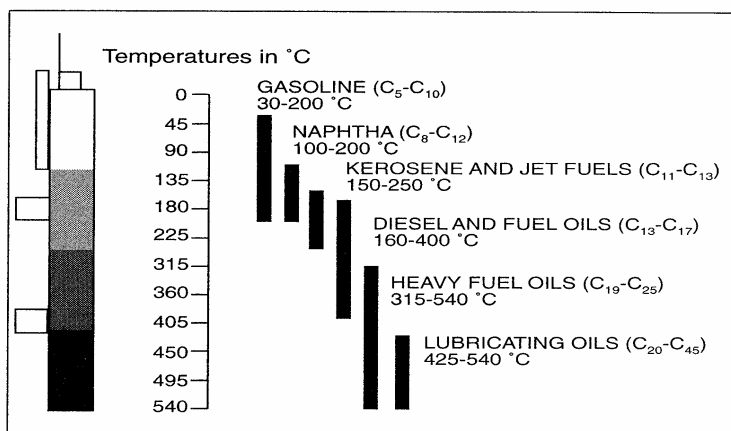


Figure 5. The boiling point ranges and carbon ranges for six common crude oil products [8].

Table 3. Composition of a 35°API-gravity crude oil [1].

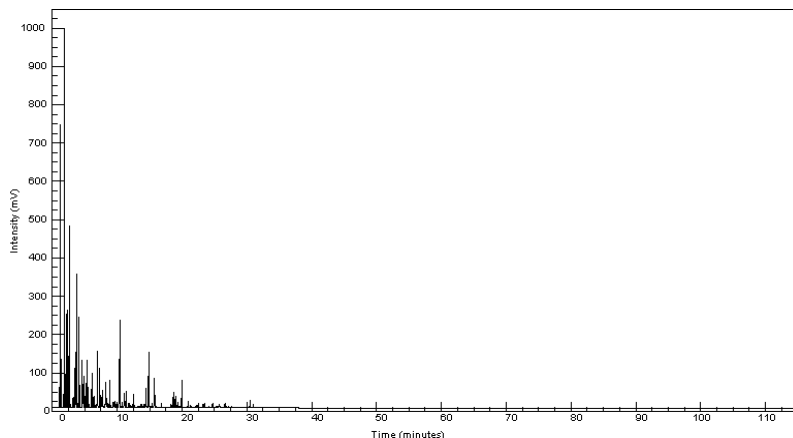
Molecular Size	Volume Percent
Gasoline (C_5-C_{10})	27
Kerosene (C_8-C_{12})	13
Diesel Fuel ($C_{13}-C_{17}$)	12
Heavy Gas Oil ($C_{19}-C_{25}$)	10
Lubricating Oil ($C_{20}-C_{45}$)	20
Residuum ($>C_{40}$)	18
Total	100

Within each of the different classes of hydrocarbons (saturates or aromatics) are compounds that have anywhere from 1 to more than 45 carbons in their chemical structure. The percentages of these compounds that are present vary among different crude oils. This characteristic can be observed by analyzing crude oils and fuels by gas chromatography.

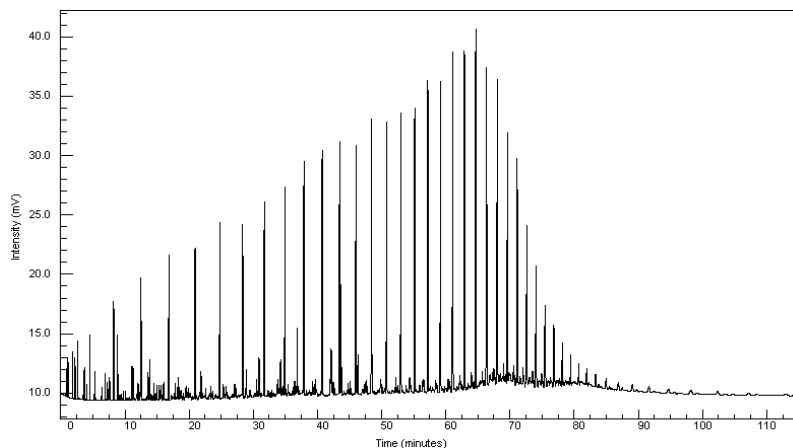
Figure 6 illustrates the distinctive gas chromatography fingerprints of gasoline, diesel, and two crude oils. Gas chromatograms, or fingerprints, give an indication of the carbon number range and hydrocarbon type (saturates versus aromatics) for the total petroleum hydrocarbons within a complex mixture. As shown in Figure 6, the diesel fuel or gasoline signatures contain hydrocarbons in the approximate range of $C_{10}-C_{24}$, and C_6-C_{12} , respectively. Therefore, their hydrocarbon ranges are always more narrow than those for crude oils. The

Widuri crude oil from Sumatra is dominated by normal alkanes or paraffins that produce a “picket fence” type pattern in the chromatograph, which is typical of waxy crude oils. On the other hand, the San Joaquin Valley (SJV) crude oil from California is dominated by a “hump” or unresolved complex mixture of hydrocarbons that is difficult for a gas chromatograph to separate. This hump is indicative of the prior biodegradation of hydrocarbons that occurred in the oil reservoir and is a common characteristic of many heavy crude oils.

Gasoline



Widuri Crude Oil



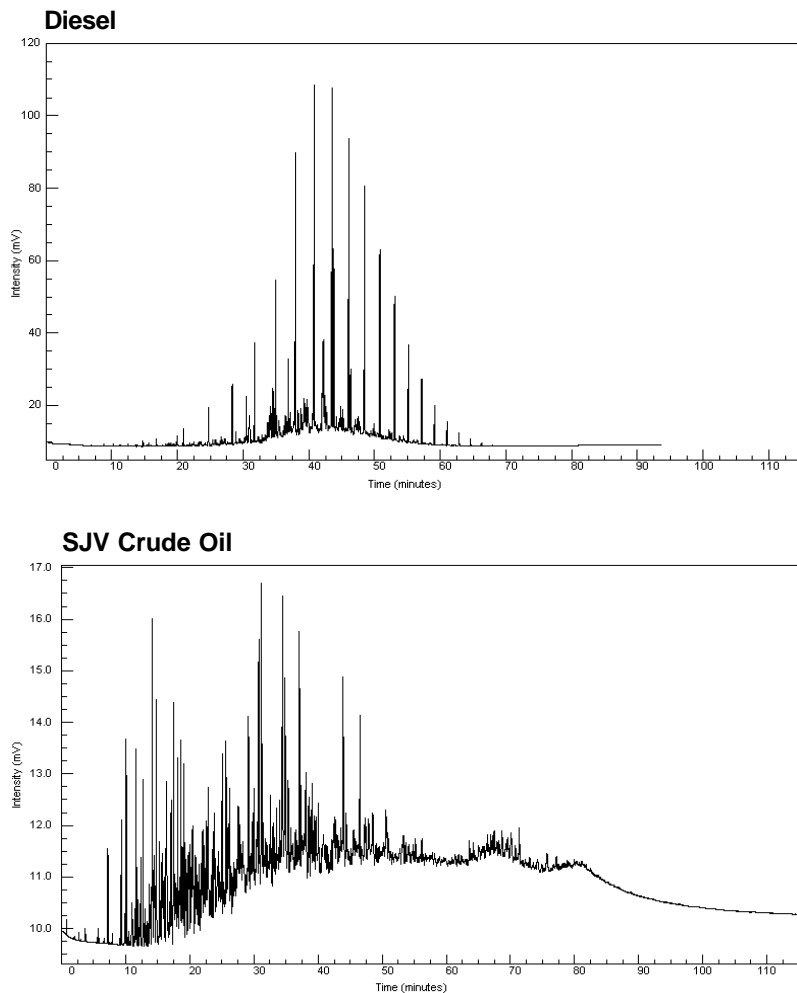


Figure 6. Gas chromatography fingerprints of gasoline, Widuri crude oil, that is enriched in normal alkanes that appear as a “picket fence” type signature, a diesel fuel and a SJV crude oil that has a “hump” that represents a large unresolved complex mixture. Units are Intensity (mV) vs. Time (minutes).

Gas Condensate Composition

Gas condensates are extracted with natural gas in a liquid form. They have a narrower carbon number range than crude oil, typically $<C_6$ - C_{15} . However,

many condensates that come directly from wells tend to have a tail of heavier hydrocarbons, while condensates that come from natural gas processing plants or from condensation in pipelines have a much narrower range. This is because some amount of processing has occurred, and these types of condensates will have carbon ranges similar to refined gasoline.

Gas chromatography fingerprints of the saturated and aromatic hydrocarbon fractions of two condensates are shown in Figure 7. These fingerprints illustrate the large degree of variability that can exist for these hydrocarbon mixtures. In particular, it is clear that Condensate A encompasses a much broader range of hydrocarbons than does Condensate B. Also, the ratio of the saturated hydrocarbons to the aromatic hydrocarbons is quite different for these two condensates, increasing from 3.2 for Condensate B to 5.8 for Condensate A.

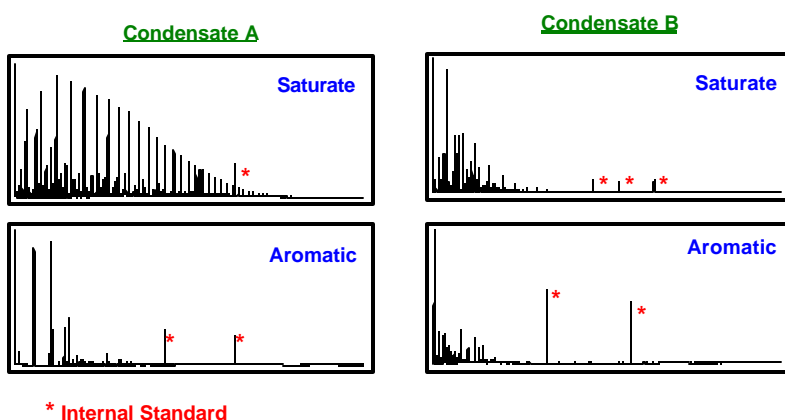


Figure 7. Gas chromatograms of condensates.

Compounds of Concern in Crude Oils and Gas Condensates

Following crude oil or condensate releases to the environment, regulators usually require that soils and/or groundwater be analyzed for TPH. Some jurisdictions may also require analysis for other compounds of concern (COCs). These COCs might include specific volatile hydrocarbons such as benzene, toluene, ethylbenzene, and xylenes; the 16 semi-volatile polyaromatic hydrocarbons that are on the EPA's priority pollutant list; and some metals. The amount of each of these COCs in crude oils and condensates as well as the implications of their presence on risk-based decision-making for E&P sites are discussed in detail in Chapters 10 through 12.

An Overview of the Physical Properties of Petroleum Hydrocarbons

The fate and transport of a hydrocarbon mixture in the environment is an important aspect of risk assessment because it determines the exposure of a human or ecological receptor to the mixture. The key physical characteristics of hydrocarbons that affect their fate and transport in the environment include:

- **Solubility in Water:** This property is arguably the most important factor that determines the transport of hydrocarbons in groundwater or surface water.
- **Volatility:** The volatility of a hydrocarbon will dictate its movement with air or other gases.
- **Density:** The density of a hydrocarbon is expressed as its API gravity, which is a measure of its specific gravity. The API gravity is inversely proportional to the specific gravity of the compound at 60°F (15°C) and is expressed as an integer [9]. It has units of degrees. As a point of reference, fresh water has an API gravity of 10°. The API gravity of refined products varies with the specific product, dropping as low as 15° for No. 6 Fuel Oil and as high as 62° for gasoline.

$$\text{API Gravity} = \frac{141.5}{\text{Specific Gravity @ } 60^{\circ}\text{F}} - 131.5$$

- **Viscosity:** This parameter is a measure of the internal resistance of a fluid to flow. Highly viscous material, like molasses, does not flow easily under the forces of gravity while water, a low viscosity material, flows readily. The viscosity of a fluid tends to decrease with an increase in temperature.
- **Pour Point:** The pour point is the temperature below which a crude oil will not flow in a horizontal tube [1]. The pour point for most oils arises from the precipitation of wax such that a pasty, plastic mass of interlocking crystals is formed. Wax-free oils have pour points that are dependent upon viscosity only and will tend to thicken to glassy materials as the temperature is reduced and the viscosity increases. Some waxy crude oils may be solid at temperatures as high as 110°F (43°C).

Crude Oil

Crude oil composition varies greatly and the differences in composition are reflected in the API gravity values for crude oils. For example, heavy API gravity oils (<20°API) have higher concentrations of asphaltenes and resins than

do light API gravity oils ($>30^\circ\text{API}$). Crude oils produced in the United States have API gravity values that range from approximately 7 to 50° [6].

Crude oil is less dense than water with a specific gravity ranging from 0.85 to 0.98 (as compared to 1.0 for water). However, because of the large differences in composition among the various crude oils, the precise specific gravity of the crudes can vary substantially.

Crude oil also tends to be a viscous liquid at surface temperatures and pressures. Surface viscosity values range from 1.9 to $19,400$ centistokes [3]. Pour point values for crude oils range from -70 to 110°F [1]. Therefore, some crude oils may be solid at typical seasonal fall and spring temperatures in the United States. The viscosity and pour point are important because they imply that many crude oils are not fluid enough to rapidly percolate through soil.

Crude oil is sparingly soluble in water, with solubility increasing with API gravity. For example, a crude oil with an API gravity of 11° had a total solubility in water of 3.5 mg/L at 25°C (77°F), whereas an oil with an API gravity of 28° had a solubility of 65 mg/L [10]. However, total solubility is dependent on temperature and the composition of the crude oil.

Condensates

Extensive physical property data are not currently available for condensates. However, in broad terms, these hydrocarbon mixtures generally exhibit an API gravity of greater than 45° . This suggests that they are not extremely viscous at normal ambient temperatures and that they are relatively volatile and soluble in water. Composition data [11] for four condensates revealed that high molecular weight alkanes can be present. The presence of these alkanes would have a tendency to increase both density (i.e., decrease API gravity) and viscosity and decrease both solubility and volatility of the hydrocarbon mixture.

Summary

The composition of crude oils and condensates can vary greatly as reflected by their class compositions, carbon ranges, and other properties such as API gravity. Composition may affect fate and transport in the environment, and therefore can impact risk-based decision-making. While it is possible to generalize as to crude oil and condensate content and properties, understanding the specific composition of oils and condensates is required before implementing risk-based decision-making at E&P sites. For this reason, the Petroleum Environmental Research Forum Project 97-08 embarked on analyzing a large number of crude oils and condensates that would be representative of those produced around the world. The data from this project are presented in the following chapters.

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Application of the Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG) Methodology to Crude Oils and Gas Condensates

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Introduction

The Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG) convened in 1993 to develop scientifically defensible information for establishing soil cleanup levels that are protective of human health at petroleum release sites [1-5]. The impetus for the formation of this group was the large disparity in cleanup standards for total petroleum hydrocarbons (TPH) in soil, and the recognition that these regulatory standards were not based on risk to human health. Active participants in this effort were the Air Force, Exxon, Shell, Chevron, the American Petroleum Institute (API), the Association of American Railroads, several state governments (Washington, Texas, Colorado, Hawaii, Louisiana, New Mexico, Massachusetts) of the United States, the United States Environmental Protection Agency (USEPA), the Department of Defense, as well as private consulting companies including EA Engineering Science and Technology and Menzie-Cura & Associates, Inc.

The use of risk-based decision-making for petroleum mixtures is complicated due to the fact that petroleum consists of several thousand individual hydrocarbons and other compounds, each with a unique set of physical and chemical characteristics including volatility and solubility. Only about 250 of these compounds have been specifically identified, and it is impossible to analyze all of the specific constituents in most petroleum products or crude oils. In response to this difficulty, the TPHCWG chose to use a fractionation approach to analyze for TPH and coupled this data with the standard risk assessment approach for deriving Tier 1 risk-based screening levels (RBSLs) described by the American Society for Testing and Materials (ASTM) [6]. Similar approaches for deriving TPH RBSLs or cleanup levels have been adopted by the States of Massachusetts, Texas, and Louisiana and incorporated into their environmental management programs for downstream sites [7-9].

The TPHCWG summarized their findings in five volumes [1-5]. This chapter provides a brief overview of their major findings, and presents new data on the composition of crude oils and condensates. Before considering the new analytical approach developed by the TPHCWG, the limitations of older TPH analytical methods are described.

Definition of Total Petroleum Hydrocarbons (TPH)

TPH is not specifically a measure of petroleum hydrocarbons, but is rather a measurement of the compounds that are soluble in certain solvents and detected by various techniques (infrared, gravimetric, gas chromatography). Many compounds other than petroleum hydrocarbons (plant waxes, soil humic material, animal fats, etc.) may be measured as TPH. Furthermore, the same sample analyzed by different TPH methods will produce different TPH concentrations due to differences in solvent type, extraction method, detection method, and quantification standards. TPH is therefore defined by the analytical method that is used to measure it.

Conventional bulk measurements of TPH in a sample are not sufficient to support a human health risk assessment. To illustrate this point, high TPH concentrations can be measured in items that clearly do not pose a risk to human health. For example, TPH concentrations have been measured in many items found in nature including peat moss (3,700 mg/kg of TPH), pine needles (19,000 mg/kg of TPH), cow manure (12,000 mg/kg of TPH), and hay (4,500 mg/kg) [10]. It has also been measured in household petroleum jelly at concentrations of 749,000 mg/kg [11]. Although these TPH concentrations are substantially greater than many existing TPH regulatory standards, none of these materials are considered a risk to human health.

Review of TPH Analytical Methods

Some of the more common methods for the analysis of TPH include: (1) Method 418.1 or Modified 418.1, (2) Method 413.1 for oil and grease, (3) Modified 8015M for Diesel-Range Organics (DRO), and (4) Modified 8015M for Gasoline-Range Organics (GRO) [12]. Method 418.1 consists of solvent extraction followed by treatment in a silica gel column and infrared spectroscopy; the modified Method 8015 for DRO and GRO are solvent extractions followed by gas chromatography (GC). If it is suspected that the sample is predominately a gasoline (i.e., volatile) fraction, purge and trap sample introduction to the gas chromatograph is often used in the determination of GRO. Method 413.1 is a gravimetric method that consists of solvent extraction, evaporation of the solvent, and a weight measurement.

In addition to these standard methods, it should be recognized that there are many permutations of these methods that have been developed and applied by

environmental regulatory agencies as well as by individual commercial analytical laboratories. These permutations evolved because, historically, no one universal method for the measurement of petroleum hydrocarbons was available for use. Many of these methods are modified versions of the gas chromatographic methods and are referred to as “modified 8015.”

Figure 1 shows the overlap between the carbon number ranges of different hydrocarbon products as well as the overlap in the corresponding TPH analytical methods [1]. For example, this figure demonstrates that a TPH method designed for gasoline range organics (i.e., C₆ to C₁₂) may report some of the hydrocarbons present in diesel fuel (i.e., C₁₀ to C₂₈). The same is also true for TPH analytical tests for diesel range organics which will identify some of the hydrocarbons present in gasoline-contaminated soils. Lastly, TPH Method 418.1 covers the complete range from gasoline through lube oil, motor oil, and grease (i.e., C₈ to C₄₀). However, crude oils may contain hydrocarbons with carbon numbers that range from C₃ to C₄₅₊ and are not fully addressed even with the use of all three TPH methods.

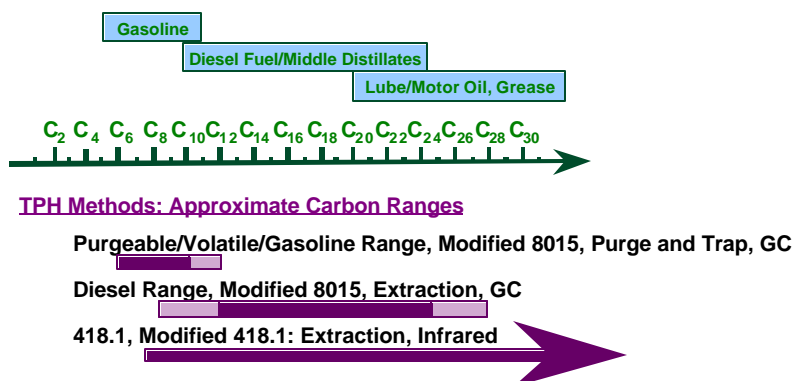


Figure 1. Carbon number ranges addressed by TPH analytical methods [1].

The hazard evaluation that is conducted as part of the risk evaluation of a site requires some level of understanding of the chemical composition of the hydrocarbons that are present in the soil and groundwater. The traditional TPH analytical techniques are not adequate to support this hazard evaluation because they provide no specific information about the hydrocarbons that are detected.

The TPHCWG Approach to Assessing Risk of TPH

The general approach of the TPHCWG consists of an assessment of risk associated with both cancer and non-cancer health effects. Some specific hydrocarbons have been identified as potential carcinogens: benzene and the

seven carcinogenic polyaromatic hydrocarbons (i.e., benz[a]anthracene, chrysene, dibenz[a,h]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, and indeno[1,2,3-cd]pyrene). These compounds are quantified separately and evaluated using standard methods of risk assessment. Discussions of cancer health effects as they relate to benzene and polyaromatic hydrocarbons are presented in Chapters 10 and 11.

Prior to the publications from the TPHCWG there was no standard method for assessing the potential risk of non-cancer health effects caused by complex mixtures of hydrocarbons or TPH. It is in this area that major innovations in the risk assessment methodology have been made. These innovations focused on the development of a better understanding of the composition of the refined products of petroleum and assigning toxicity, fate, and transport characteristics to hydrocarbon fractions.

The complexity of petroleum hydrocarbons represented the major challenge to the TPHCWG. Table 1 illustrates that this complexity is due to the number of possible isomers that may be present in higher molecular weight mixtures such as diesel or crude oils.

Table 1. Possible number of paraffin isomers for each size molecule [13].

Size	Isomers	Size	Isomers
C ₁ , C ₂ , C ₃	1 Each	C ₁₀	75
C ₄	2	C ₁₁	159
C ₅	3	C ₁₂	355
C ₆	5	C ₁₃	802
C ₇	9	C ₁₅	4,347
C ₈	18	C ₁₈	60,523
C ₉	35	C ₂₅	36,797,588

Because it is impossible to analyze complex petroleum hydrocarbon mixtures for all of their constituents, and no one compound could possibly act as a surrogate for these mixtures, the TPHCWG chose to use a fractionation approach to assess oil composition. The first step in this fractionation approach was to separate the hydrocarbons into two groups based on chemical structure (i.e., aliphatic hydrocarbons and aromatic hydrocarbons). Once segregated into these groups, the aliphatic hydrocarbons were separated into six carbon number fractions and the aromatic hydrocarbons into seven carbon number fractions (Figure 2). Each of the 13 fractions was then treated as if it were a separate compound in the environment.

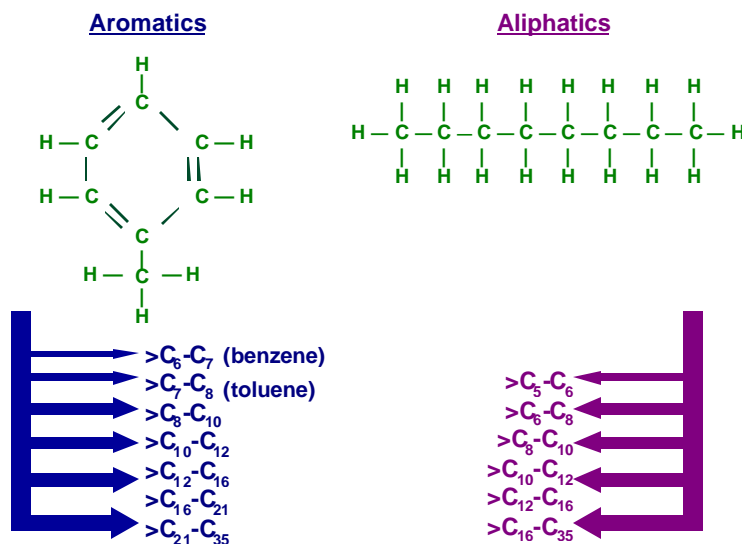


Figure 2. TPH Fractionation: Separation of chemical groups into carbon-number ranges.

The TPHCWG developed an analytical technique that is based on USEPA SW-846 [13] methods for separating hydrocarbons into fractions using GC techniques. First, the petroleum hydrocarbon or pentane extract of a soil is separated into aliphatic and aromatic hydrocarbon fractions. This chemical separation is based on an alumina column procedure (SW-846 USEPA Method 3611) or a silica gel column procedure (SW-846 USEPA Method 3630) [13]. The aliphatic and aromatic hydrocarbon fractions are analyzed separately by GC and quantified by summing the signals within a series of specific carbon ranges. The GC is equipped with a boiling point (i.e., non-polar capillary) column [1].

The 13 TPH fractions are based on “equivalent carbon” (EC) numbers rather than “carbon numbers.” ECs are related to the boiling point of individual compounds in a boiling point GC column, normalized to the boiling point of a normal alkane. Thus, for compounds where only a boiling point is known, the EC can be readily calculated. For example, the EC of benzene is 6.5 because its boiling point and GC retention time are approximately halfway between those of n-hexane and n-heptane. Benzene’s EC number is greater than that of n-hexane because its ring structure results in a higher boiling point. The TPHCWG chose the concept of EC numbers because these values are more logically related to compound mobility in the environment than carbon numbers [3].

USEPA Method 8260 is required to analyze for benzene (the only hydrocarbon in the aromatic C₆-C₇ fraction), and toluene (the only hydrocarbon in the aromatic C₇-C₈ fraction), rather than using the TPHCWG analytical method. The TPHCWG analytical method is provided in the Appendix.

The Basis for Defining 13 TPH Fractions

The EC fractions were identified by selecting groups of hydrocarbons that have similar fate and transport properties, such as solubility and vapor pressure. This was done because of the important role that fate and transport play in determining the exposure of a receptor to a site contaminant. For example, highly soluble petroleum compounds are more likely to migrate to groundwater and represent potential risk to humans via the consumption of drinking water. By choosing fate and transport criteria for the definition of the fractions, the TPHCWG ensured that the risk assessment would properly capture the fraction of the hydrocarbon mixture that would be present at the point of exposure for the variety of exposure pathway-receptor combinations that might be present at a site.

Aliphatic and aromatic hydrocarbon fractions were considered separately because their solubility and other fate and transport characteristics are so dramatically different (Table 2). Within each of these groups, the major differences in fate and transport properties were related to the EC numbers of the compounds. As shown in Table 2 and Figure 3, the properties of the compounds (i.e., solubility, vapor pressure) and their modeled environmental behavior [i.e., coefficient for partitioning to organic carbon (K_{oc}) from soil to water (LF_{sw})] change by an order-of-magnitude or more between the different EC number fractions.

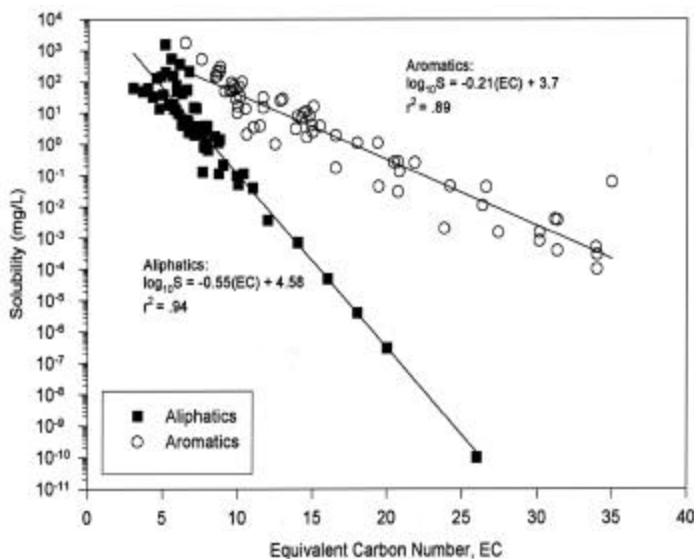
Table 2. Fate and transport characteristics of TPH fractions (based on EC number) [3].

	Solubility (mg/L)	Vapor Pressure (Atm)	Log Koc	H (cm ³ /cm ³)	LFsw (mg/L)/(mg/kg)
Aliphatic Fractions					
C ₅ -C ₆	3.6E+01	3.5E-01	3.0E+00	3.40E+01	6.25E-03
>C ₆ -C ₈	5.4E+00	6.3E-02	3.6E+00	5.10E+01	1.73E-03
>C ₈ -C ₁₀	4.3E-01	6.3E-03	4.8E+00	8.20E+01	2.51E-04
>C ₁₀ -C ₁₂	3.4E-02	6.3E-04	5.9E+00	1.30E+02	3.26E-05
>C ₁₂ -C ₁₆	7.6E-04	4.8E-05	6.7E+00	5.40E+02	1.64E-06
>C ₁₆ -C ₃₅	1.5E-06	1.1E-06	8.6E+00	1.10E+02	8.26E-09
Aromatic Fractions					
C ₆ -C ₇ (Benzene)	1.8E+03	1.3E-01	1.9E+00	2.25E-01	9.00E-02
>C ₇ -C ₈ (Toluene)	5.2E+02	3.8E-02	2.4E+00	2.70E-01	3.37E-02
>C ₈ -C ₁₀	6.5E+01	6.3E-03	2.9E+00	4.90E-01	5.16E-03
>C ₁₀ -C ₁₂	2.5E+01	6.3E-04	3.2E+00	1.40E-01	3.28E-03
>C ₁₂ -C ₁₆	5.8E+00	4.8E-05	3.8E+00	5.40E-02	1.64E-03
>C ₁₆ -C ₂₁	5.1E-01	7.6E-06	4.2E+00	1.20E-02	5.21E-04
>C ₂₁ -C ₃₅	2.9E-02	1.6E-08	5.1E+00	8.20E-05	6.56E-05

Koc = Carbon-water sorption coefficient

LFsw = Leaching factor from soil to water

H = Henry's Law constant

**Figure 3.** Solubility vs. equivalent carbon number for aromatics and aliphatics [3].

Toxicity criteria were developed for each fraction as shown in Table 3. The methodology used by the USEPA and the TPHCWG for developing the reference doses (RfDs) and reference concentrations (RfCs) is described in detail in Chapter 7.

Table 3. Toxicity criteria for TPH fractions [4].

Equivalent Carbon Number Range	Oral RfD (mg/kg/day)	Inhalation RfC (mg/m³)
Aliphatic <C ₆ >C ₆ -C ₈	5.0	18.4
Aromatic C ₆ -C ₇ (Benzene) >C ₇ -C ₈ (Toluene)	0.2	0.4
Aliphatic >C ₈ -C ₁₀ >C ₁₀ -C ₁₂ >C ₁₂ -C ₁₆	0.1	1.0
Aromatic >C ₈ -C ₁₀ >C ₁₀ -C ₁₂ >C ₁₂ -C ₁₆	0.04	0.2
Aliphatic >C ₁₆ -C ₃₅	2.0	NA
Aromatic >C ₁₆ -C ₃₅	0.03	NA

NA = Not available

Adapting the TPHCWG Analytical Methodology to Crude Oils

The original TPHCWG approach does not include hydrocarbons greater than carbon number 28 (C₂₈), but has been modified to include up to C₃₅ [3]. This is appropriate for most refined products, such as gasoline and diesel, as well as for condensates. However, some crude oils with very low API gravity values may contain as much as 50 to 60% hydrocarbons >C₃₅. Therefore, the TPHCWG analytical methodology was further modified so that hydrocarbons up to C₄₄ could be fractionated and detected by GC (as described in Chapter 5). Figure 4 presents the data for 15 different crude oil samples plus a diesel sample using the extended GC analytical method. From this figure, it can be seen that approximately 45 to 80% of the hydrocarbons in crude oil can be detected using a gas chromatograph (i.e., EC numbers from C₆ to C₄₄).

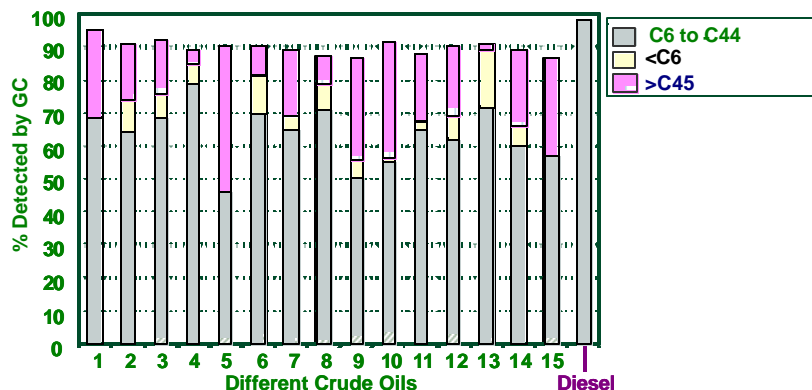


Figure 4. Mass balance obtained for crude oils using a modified TPHCWG analytical method and distillation data.

The remaining hydrocarbons fall into two groups: those $<C_6$ or those $>C_{44}$. These ranges are typically quantified using distillation to determine the entire composition of a crude oil. The hydrocarbon fraction with carbon numbers greater than C_{44} is sometimes called the vacuum residuum, because it contains the compounds remaining after the vacuum distillation of crude oil. The less than C_6 fraction is lighter than gasoline and is predominately the component of natural gas. The amounts of hydrocarbons $<C_6$ and $>C_{44}$ (obtained from distillation) for each crude oil are also shown in Figure 4. The addition of all three molecular weight ranges accounts for more than 85% of the compounds within crude oils. At the same time, greater than 95% of diesel oil can be detected by the TPHCWG analytical method alone, further reinforcing that the TPHCWG method adequately quantifies refined products such as diesel.

There are no standard USEPA analytical methods available for quantifying either the $<C_6$ or the $>C_{44}$ fraction (vacuum residuum). Because the $<C_6$ fraction is generally lost to volatilization after a crude oil release, it is likely to be unnecessary to quantify this fraction for assessing potential health risks for soil exposures. On the other hand, the fate and transport characteristics of the $>C_{44}$ fraction or vacuum residuum (see Table 4) indicate that it may remain in soils even after extensive weathering of an oil has occurred.

The vacuum residuum fraction of a crude oil is comprised of very large molecules (those boiling above 600°C) that are not well characterized as to their compositional make up, but it is known to contain a mixture of aliphatics, aromatics, metals, and asphaltenes. Because of the complex nature, limited

mobility, and the small amount of published toxicity data on this fraction, a decision was made to evaluate it as a single fraction, rather than trying to separate it into its aliphatic and aromatic components. The amount of vacuum residuum in 800 crude oils from the United States is shown in Figure 5 [14].

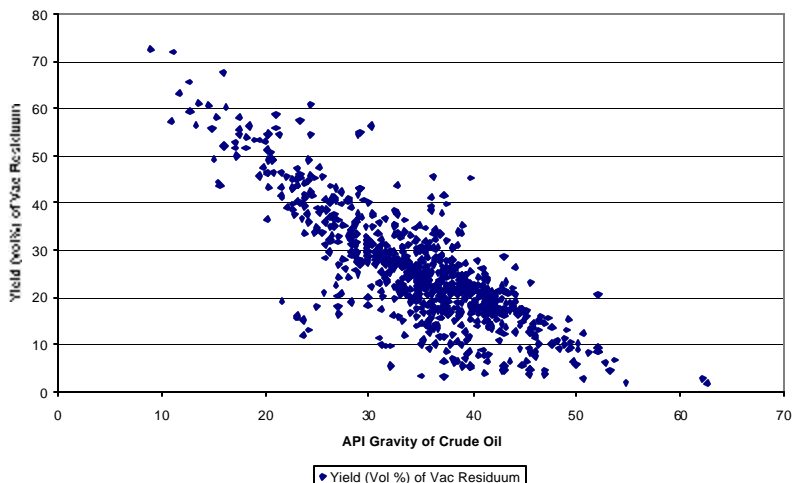


Figure 5. The yield of vacuum residuum in 800 crude oils produced in the United States [14].

To determine the mass of vacuum residuum in a crude oil, three approaches can be used: (1) using the known amount of vacuum residuum present in a crude oil as determined by distillation; (2) estimating the amount of vacuum residuum from the API gravity; and (3) assuming that all material not accounted for by GC is vacuum residuum. The first method is probably the most reliable, but distillation data are not always available and may be costly to obtain. The second method provides a rough approximation since it uses the slope of the line that is fit through the data shown in Figure 5, so that:

$$\% \text{ Yield of Vacuum Residuum} = -1.253(\text{API Gravity}) + 69.32$$

This equation has a R^2 value of 0.66. The third method is probably the least reliable, but may be an acceptable approach if neither distillation nor API gravity data are available.

Summary of Recommended Changes to the TPHCWG for Crude Oil Analyses

Figure 6 presents a modification of the TPHCWG approach for the aliphatic and aromatic carbon number fractions that can be used to conduct a risk-based assessment of the TPH that is associated with crude oils. The major changes made to the original carbon number fractions of the TPHCWG shown in Figure 2 are as follows:

- (1) The $>C_{21}$ to C_{35} aromatic carbon number fraction was replaced by a $>C_{21}$ to C_{44} carbon number fraction.
- (2) The $>C_{16}$ to C_{35} aliphatic carbon number fraction was replaced by a $>C_{16}$ to C_{44} carbon number fraction.
- (3) A $>C_{44}$ carbon number fraction was added that included both aliphatic and aromatic hydrocarbons.

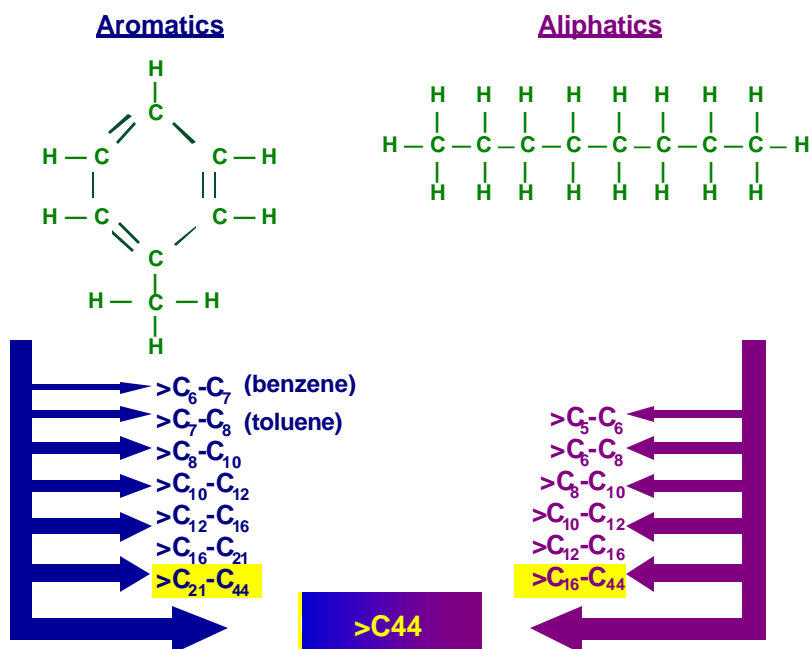


Figure 6. Aliphatic and aromatic carbon number fractions for the assessment of risk associated with crude oil TPH (highlighted fractions are different than fractions of TPHCWG).

The fate and transport characteristics for the C_{35} - C_{44} and the $>C_{44}$ fractions are presented in Table 4. The toxicity characteristics were evaluated for these fractions as described in detail in Chapter 7. Because of the fate and transport characteristics of the C_{44} fraction, the only exposure pathway of concern will be direct contact with surface soil.

Table 4. Fate and transport characteristics of additional TPH fractions (based on equivalent carbon number) [11].

	Solubility (mg/L)	Vapor Pressure (Atm)	koc (cm ³ /g)	H (cm ³ /cm ³)	LFsw (mg/L)/ (mg/kg)
Aliphatic Fractions					
$>C_{16}$ - C_{44}	1.3E-06	7.6E-06	1.00E+09	6.40E+03	8.26E-09
Aromatic Fractions					
$>C_{21}$ - C_{44}	6.6E-03	4.4E-09	1.26E+05	6.80E-04	6.56E-05
Vacuum Residuum					
$>C_{44}$	1.0E-04	NA	5.01E+05	4.10E-08	1.65E-05

Comparison of Crude Oil Composition With Some Petroleum Products

Figure 7 provides a comparison of the distribution of the carbon number fractions for a single analysis of four different mixtures of hydrocarbons (i.e., samples of gasoline, diesel, Vaseline[®], and a 34°API gravity crude oil). Not surprisingly, the gasoline is dominated by the lower carbon number aliphatic and aromatic hydrocarbon fractions ($>C_6$ to C_{10} aromatics and $>C_6$ to C_8 aliphatics). On the other extreme is the Vaseline[®] which consists almost exclusively of the aliphatic fraction, $>C_{16}$ (baby oil is similar in composition). Lastly, as expected, the hydrocarbon fractions in a crude oil cover the full range of carbon numbers for both the aliphatic and aromatic fractions.

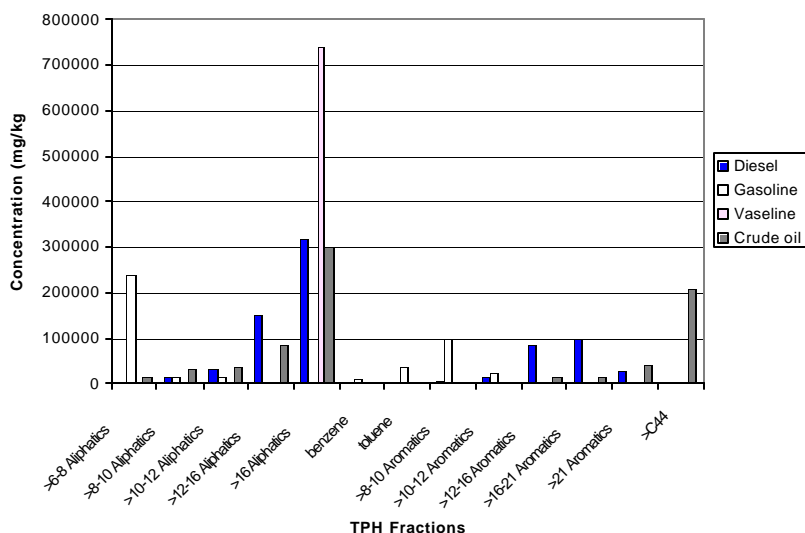


Figure 7. Comparison of the distribution of carbon number fractions in crude oil and selected products.

Analytical Results for Crude Oils

As part of a joint industry Petroleum Environmental Research Forum project (PERF 97-08), approximately 70 crude oils were analyzed using the modified TPHCWG fractionation method. These oils were selected to cover a wide range of API gravity values and geographical locations, and were contributed by Chevron (33 oils), Exxon (15 oils), Shell (17 oils), and Unocal (5 oils). Figure 8 illustrates the sampling locations for 70 crude oils, with 30 of these oils being from North America. The API gravity for these crude oils range from 8.8° to 46.4°.

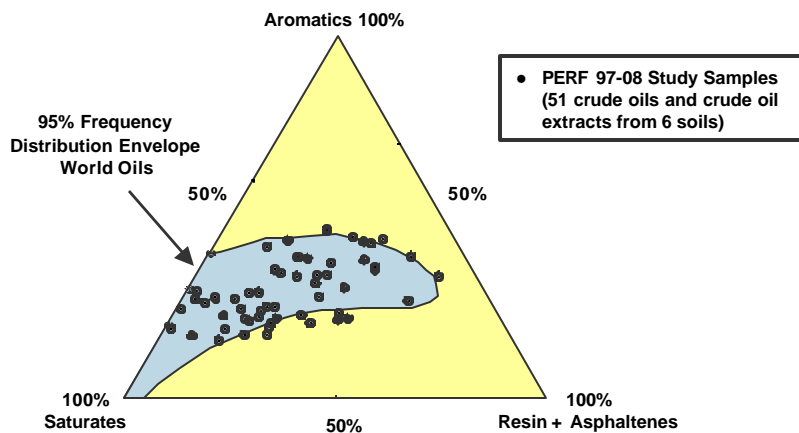


Figure 9. Triangular plot comparison of PERF oil composition to that of 636 oils from around the world.

The crude oil composition data obtained from the modified TPHCWG fractionation method are shown in Table 5 for 70 crude oils. The $>C_{44}$ data were obtained for a smaller set of the crude oils. The $>C_{44}$ data were obtained by either vacuum distillation or were calculated using the API gravity correlation to vacuum residuum. Table 5 also contains the results of USEPA Method 8260 for volatile organic chemicals. The benzene and toluene values obtained by Method 8260 are presented rather than the C_6-C_7 and C_7-C_8 aromatic data obtained by the TPHCWG analytical method because they are considered more reliable. As discussed in Chapter 11, benzene is usually evaluated separately in risk-based decision-making because it is a carcinogen. The polyaromatic hydrocarbon compositions of 60 crude oils are presented in Chapter 10.

Table 5. TPH fraction composition of 70 crude oils.

	Mean (mg/kg)	Minimum (mg/kg)	Maximum (mg/kg)	Standard Deviation (mg/kg)	Number of Non- Detects	Total Sample Points
TPH Fractions						
>C ₆ -C ₈ Aliphatics	36,000	24.5	220,000	37,000	3	70
>C ₈ -C ₁₀ Aliphatics	48,000	760	140,000	36,000	0	70
>C ₁₀ -C ₁₂ Aliphatics	36,000	4,100	73,000	18,000	0	70
>C ₁₂ -C ₁₆ Aliphatics	83,000	14,000	180,000	37,000	0	70
>C ₁₆ -C ₄₄ Aliphatics	200,000	18,000	410,000	74,000	0	70
>C ₈ -C ₁₀ Aromatics	11,000	68	48,000	10,000	0	70
>C ₁₀ -C ₁₂ Aromatics	9,600	410	31,000	5,600	0	70
>C ₁₂ -C ₁₆ Aromatics	31,000	10,000	94,000	16,000	0	70
>C ₁₆ -C ₂₁ Aromatics	39,000	7,200	72,000	15,000	0	70
>C ₂₁ -C ₄₄ Aromatics	85,000	1,600	220,000	54,000	0	70
>C ₄₄	230,000	25	570,000	160,000	1	41
Volatiles – EPA8260						
n-Hexane	4,900	73	16,000	4,300	0	15
Benzene (>C ₆ -C ₇ Aromatics)	1,300	0.16*	5,900	1,600	3	71
Toluene (>C ₇ -C ₈ Aromatics)	4,500	30	25,000	5,700	0	71
Ethylbenzene	1,100	1.9	4,600	1,023	3	71
Total Xylenes	6,500	7.3	27,900	6,600	0	71

*This value represents one-half the detection limit for benzene.

Analytical Results for Gas Condensates

Fourteen condensate samples were also analyzed by the modified TPHCWG analytical method as part of the PERF study. Ten samples were contributed by Arthur D. Little, Inc., and four were contributed by the Gas Technology Institute. The API gravity for these condensates range from 45° to 70.1°.

The composition of the condensates is shown in Table 6. No hydrocarbons >C₄₄ were detected. No aromatic hydrocarbons >C₂₁ were found in 9 of the 14 condensates. Table 6 also contains the results of USEPA Method 8260 for the volatile organic chemicals: benzene, toluene, ethylbenzene, and xylenes. The polyaromatic hydrocarbon data for 10 condensates are presented in Chapter 10.

Table 6. TPH fraction composition of 14 gas condensates.

	Mean (mg/kg)	Minimum (mg/kg)	Maximum (mg/kg)	Standard Deviation (mg/kg)	Number of Non- Detects	Total Sample Points
TPH Fractions						
>C ₆ -C ₈ Aliphatics	218,231	56,000	670,394	48,000	0	14
>C ₈ -C ₁₀ Aliphatics	154,296	85,000	230,430	46,550	0	14
>C ₁₀ -C ₁₂ Aliphatics	74,117	569	130,000	37,000	0	14
>C ₁₂ -C ₁₆ Aliphatics	69,778	ND	210,000	65,000	1	14
>C ₁₆ -C ₄₄ Aliphatics	44,936	ND	200,000	63,000	2	14
>C ₈ -C ₁₀ Aromatics	60,577	24270	117,399	29,000	0	14
>C ₁₀ -C ₁₂ Aromatics	19,837	ND	29,000	7,500	1	14
>C ₁₂ -C ₁₆ Aromatics	15,633	ND	43,000	13,500	1	14
>C ₁₆ -C ₂₁ Aromatics	6,089	ND	28,000	9,800	4	14
>C ₂₁ -C ₄₄ Aromatics	3,707	ND	20,000	7,100	9	14
>C ₄₄		ND	ND		14	14
Volatiles – EPA8260						
Benzene (>C ₆ -C ₇ Aromatics)	9,500	2,500	24,000	7,900	0	10
Toluene (>C ₇ -C ₈ Aromatics)	31,000	14,000	53,000	15,000	0	10
Ethylbenzene	5,000	1,400	6,700	2,000	0	10
Total Xylenes	33,000	8,200	61,000	18,000	0	10

Summary

Most TPH analytical methods are not adequate for assessing potential risk to human health because they are non-specific and provide little information on the types of compounds present in terms of class or carbon range. The TPHCWG developed a risk evaluation approach for complex petroleum hydrocarbon products, based on an analytical method that divides the complex mixture into several distinct carbon number fractions coupled with standard risk assessment equations for assessing human exposure. With slight modifications, the TPHCWG analytical method can be used to assess the hydrocarbon content of crude oils. These modifications include extending the TPHCWG analytical method to C₄₄ and determining the fraction >C₄₄ using one of three methods. However, some regulatory agencies may opt to omit hydrocarbons >C₄₄ in risk assessments due to their lack of mobility in the environment.

TPH fraction data derived using the modified TPHCWG methodology can be used to estimate potential non-carcinogenic human health risks. Since crude oils vary widely in composition, 70 different crude oils were analyzed that were representative of all the types of crude oils produced around the world. Data for the equivalent carbon fractions and BTEX were presented. TPH RBSLs derived using these data are presented in Chapter 8. Chapters 10 and 11 present more

details on risk analysis of the indicator carcinogenic hydrocarbons, benzene and some polyaromatic hydrocarbons.

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Performance of TPHCWG Analytical Method for Crude Oils in Soils

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Introduction

In evaluating the application of the TPHCWG analytical method (see Appendix) to crude oil and crude oil impacted sites, several important factors affecting method performance were considered. The factors investigated included soil type, oil characteristics (unlike refined products, crude oils vary greatly), extraction procedures, fractionation procedures (separation of the extract into aliphatic and aromatic hydrocarbons), and chromatographic conditions. Each of these factors is described in the paragraphs below.

Soils

Soil types investigated were sand, loam, and clay. Table 1 summarizes the soil samples and their characteristics. The petroleum hydrocarbons that were added to the soils included aged hydrocarbons (residual from historic releases) and fresh oil added at the laboratory.

Table 1. Soil and hydrocarbon type used to evaluate the TPHCWG method.

Sample	Soil Type	Previous Oil	Lab Spike (% by Weight)	Oil Type (°API)
1	Sand	Remediated <1% TPH	2%	38
2	Sand	None	1.5%	11
3	Loam	None	4%	15
4	Loam	None	2%	34
5	Clay	Remediated <1% TPH	3%	25
6	Clay	Remediated <1% TPH	1%	22

Oils

Six different crude oils, in addition to the historic, aged hydrocarbons, were used for the study. The American Petroleum Institute (API) gravity (°) of the oils ranged from 11° to 38°. Oil was spiked into each soil sample to achieve a TPH

concentration of between 1.5 and 4% oil by weight. Total recovery of oil was calculated against an identical direct analysis of the oil. Heavier oils, with lower API gravity values, tend to have greater proportions of C_{28} material, while some lighter oils, with higher API values, tend to have greater proportions of paraffins (normal alkanes). These characteristics may bias the analysis of crude oils using the current TPHCWG method.

Extraction

Four extraction procedures were investigated. If different extraction procedures provided comparable results, then commercial laboratories would have greater freedom in meeting a performance-based criteria method, and data users would have greater opportunity to compare data from different sources.

- The TPHCWG method is a performance based method that recommends the extraction of 10 g of soil (dried with NaSO_4) with 10 mL of pentane by vortexing or shaking for a minimum of 2 minutes (sometimes an overnight shaker is used). An aliquot is withdrawn from the final extract for analysis without concentrating the sample.
- The TPHCWG method was modified to use methylene chloride instead of pentane. This requires the additional step of exchanging the extract to pentane before column fractionation; this also involves minimal concentration of the extracted material.
- Soxhlet extraction (USEPA Method 3541 [1]) requires the extraction of a 5 to 10 g soil sample (dried with NaSO_4) with 100 mL of heated/boiling solvent (usually methylene chloride); this procedure requires extract concentration to maintain detection limits.
- Ultrasonic extraction (USEPA Method 3550B [1]) employs sequential extractions of soil with room temperature solvent (e.g., methylene chloride). This method uses the largest volume of solvent, thus requiring the most concentration, usually performed by Kuderna-Danish (KD) concentration. This method has the advantage of increased oil recovery because of the sequential extractions. Sequential extractions could be applied to other methods for the same purpose; however, transfer and volatile losses are possible.

Fractionation

Four different fractionation (separation of the extract into aliphatic and aromatic) procedures were evaluated. Two procedures are provided in the TPHCWG method based on modified USEPA Methods 3630 Silica Gel and

3611 Alumina Separations [1]. The other two procedures are modifications of USEPA Method 3630 [1], Silica Gel Separation.

The fractionation methods were evaluated in two ways. First, a laboratory standard containing normal alkanes, benzene, toluene, ethylbenzene, and xylenes (BTEX), and the 16 priority pollutant polyaromatic hydrocarbons (PAHs) was prepared and fractionated by each procedure. Second, direct analysis of non-fractionated oils and extracted soil residues were compared to post-fractionation data to monitor mass balance (aliphatic/aromatic ratios) and extraction recovery efficiency.

The TPHCWG provides two procedures for the separation of hydrocarbons into aliphatic and aromatic class based extracts. These employ alumina or silica gel chromatography. Both methods use small volumes for ease, expense, and to alleviate the need to concentrate extracts. The TPHCWG procedures plus the two additional procedures are summarized below.

- Alumina chromatography uses 4 g activated alumina as the solid phase and pentane to elute the aliphatic fraction and methylene chloride for the aromatics.
- Silica gel chromatography uses 2 g activated silica gel (75-250 mesh) as the solid phase and pentane (to elute the aliphatic fraction) and 1:1 acetone:methylene chloride (to elute the aromatic fraction) as the mobile phase, or eluents.
- USEPA Method 3630 [1] was modified to use 11 g silica gel as the solid phase and pentane (to elute the aliphatics) and 1:1 pentane:methylene chloride (to elute the aromatics). This method resulted in greater volumes of solvent being used that would require extract concentration to maintain detection limits.
- USEPA Method 3630 [1] was further modified by using a high performance liquid chromatographic system to optimize the aliphatic/aromatic separation. This method used a packed silica gel column with a dual-solvent gradient elution program using pentane and methylene chloride. Sample collection windows for the aliphatic and aromatic compounds were determined using aliphatic and aromatic control standards.

Chromatographic Conditions

Chromatographic conditions for the gas chromatography with flame ionization detection (GC/GFID) described in the TPHCWG method were designed for use with refined petroleum products such as gasoline and diesel. These conditions

may not be optimal for analysis of crude oils and were examined in this study. Chromatographic conditions affecting the analysis of crude oil that were investigated include loading capacity, effective carbon elution range, and mass discrimination.

Results

This study was designed to evaluate the impact of sample processing on the analysis of crude oil for TPHCWG method results. The critical elements in the performance of this method were identified as extraction, fractionation of the extract into aliphatics and aromatics, and GC/FID separation (chromatography).

Extraction

Table 2 compares the total recoverable petroleum hydrocarbon results for the six soil types and four extraction techniques. Pentane does appear to be an adequate solvent for extracting crude oils from soil, achieving recoveries similar to those for methylene chloride. However, these results further demonstrate that TPH is method defined, with each solvent and extraction procedure giving somewhat different results. Laboratories should be flexible in their performance of the method and evaluate potential bias by analyzing a matrix spike and matrix spike duplicate with each analytical batch.

Table 2. Total recovered petroleum hydrocarbons (mg/kg).

Method	Sample					
	1-Sand	2-Sand	3-Loam	4-Loam	5-Clay	6-Clay
Concentration of Added Oil in Soil	30,000	15,000	40,000	20,000	40,000	20,000
Vortex – Pentane	24,700	8,160	21,700	15,800	30,600	7,250
Vortex – Methylene Chloride	23,200	7,500	33,700	16,400	43,000	11,200
Soxhlet – Methylene Chloride	20,800	7,170	18,100	15,100	41,100	14,400
Sonication – Methylene Chloride	NA	6,730	19,400	14,900	45,800	20,800

NA – Sample was lost in lab and could not be replaced.

Fractionation

All four fractionation procedures were evaluated using a laboratory standard containing normal alkanes, BTEX, and the 16 priority pollutant PAHs. As with all fractionation procedures, it is imperative that the effectiveness of the separation column be tested prior to any sample analysis. Several factors influence the efficiency of a fractionation column to resolve compound classes. They include activation/deactivation of the silica or alumina, type of solvents, type of oil, and column overloading. Potential deactivation of the pre-packaged

columns with moisture is a potential problem and they are therefore not recommended.

For comparison purposes, GC/FID chromatograms for the TPHCWG and Modified USEPA Method 3630 fractionation procedures are provided in Figures 1a and 1b, respectively. Figure 1a shows some compound class carryover observed in the TPHCWG fractionation procedure which demonstrates the need for the laboratory to monitor the fractionation efficiency carefully. When this situation is encountered, the column must be reactivated before any samples are analyzed.

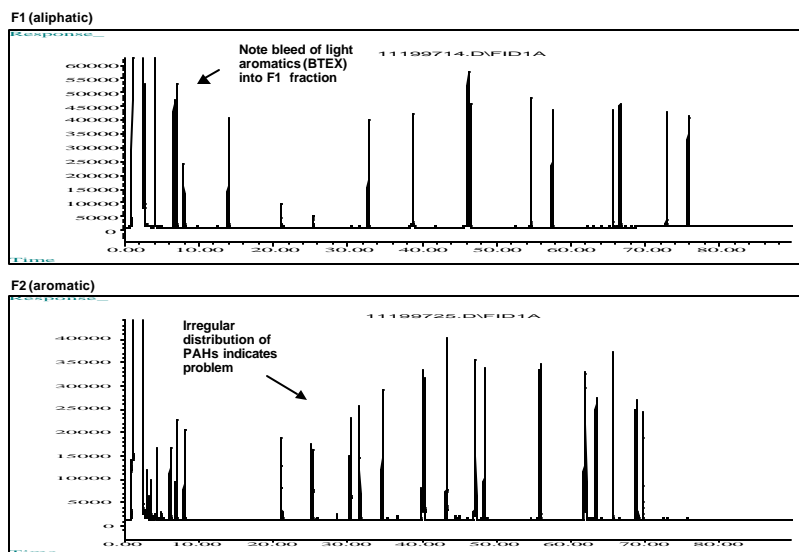


Figure 1a. The sample fractionation procedure must be carefully monitored with aliphatic and aromatic standards. This is an example of a separation performed using pre-packaged columns; less than 1 mg total material was loaded onto the column. The column was either improperly activated or overloaded.

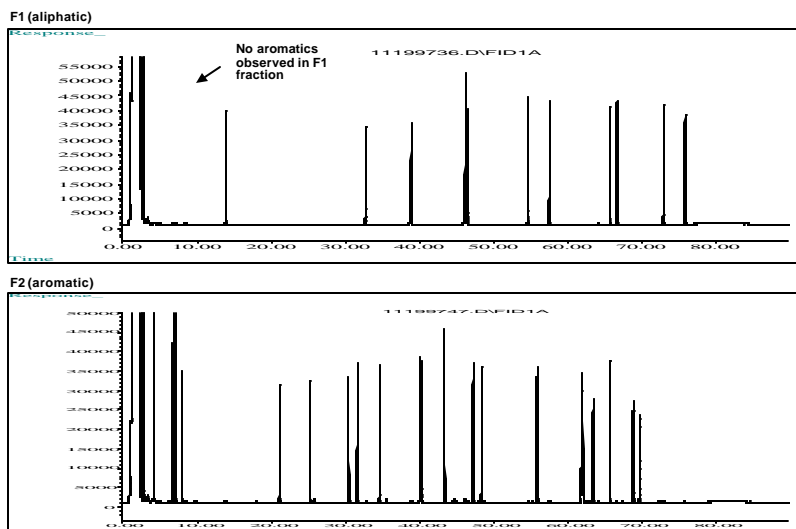


Figure 1b. Fractionation should be monitored with a check standard. (This separation performed following modified USEPA Method 3630, Silica Gel Separation.)

Figure 1b shows proper fractionation with minimal compound class carryover. When proper activation is achieved, no problems are encountered with the modified methods using columns prepared by the laboratory. The two modifications of USEPA Method 3630, both open column and HPLC, provided comparable results. These procedures employ available technology and are easily performed by most environmental laboratories. The performance-based nature of this method should allow laboratories to produce comparable results through careful modification of USEPA Method 3630. Table 3 compares the results of the four fractionation procedures on two soil samples.

Table 3a. High API gravity oil in sand.

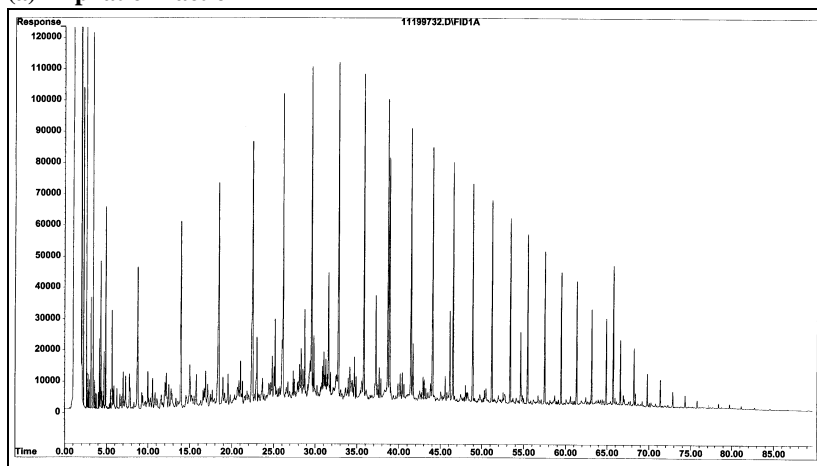
Method	Total Aliphatic (mg/kg)	Total Aromatic (mg/kg)	% Aliphatic
TPHCWG – Alumina	13,000	3,100	81
TPHCWG – Silica	12,000	5,000	70
USEPA 3630 – Silica	11,000	5,300	67
USEPA 3630 – Silica – HPLC	11,000	4,700	70

Table 3b. Low API gravity oil in sand.

Method	Total Aliphatic (mg/kg)	Total Aromatic (mg/kg)	% Aliphatic
TPHCWG – Alumina	5,400	3,700	59
TPHCWG – Silica	4,900	4,000	55
USEPA 3630 – Silica	4,200	4,100	51
USEPA 3630 – Silica – HPLC	4,100	4,000	50

As with any fractionation method for compound class separation, it is essential for laboratories to evaluate and confirm that the fractionation method used is adequate for crude oils by using a column calibration standard. The standard used in this analysis (or a similar one) should be adopted by method users as a requirement for the demonstration of method performance.

Visual analysis of the aliphatic and aromatic fractions of crude oils can help identify problems with the fractionation procedures. The aliphatic fraction has a typical alkane distribution characteristic of this compound class, as shown in Figure 2a.

(a) Aliphatic Fraction

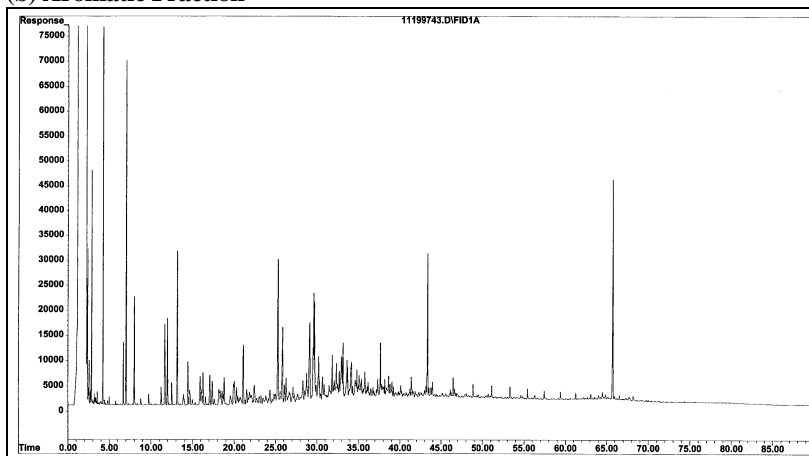
(b) Aromatic Fraction

Figure 2. Aliphatic (a) and Aromatic (b) fractions of high API gravity crude oil.

However, in biodegraded oils (Figure 3a, low API gravity) this aliphatic hydrocarbon pattern may not be as evident due to the biodegradation of the n-alkanes. In the case of the aromatic fraction, the high API gravity oil demonstrates a characteristic pattern of one, two, and three ring aromatics (Figure 2b); however, in the low API gravity oil the characteristic pattern is degraded and replaced by an unresolved aromatic complex mixture (Figure 3b). Identification of carryover in the low API gravity oil is more difficult than the more common lighter crude oils, therefore careful analysis of quality control samples is critical for the successful application of this procedure. For waxy crude oils, the carryover of high molecular weight n-alkanes is a frequent problem that can only be identified by evaluating the chromatograms.

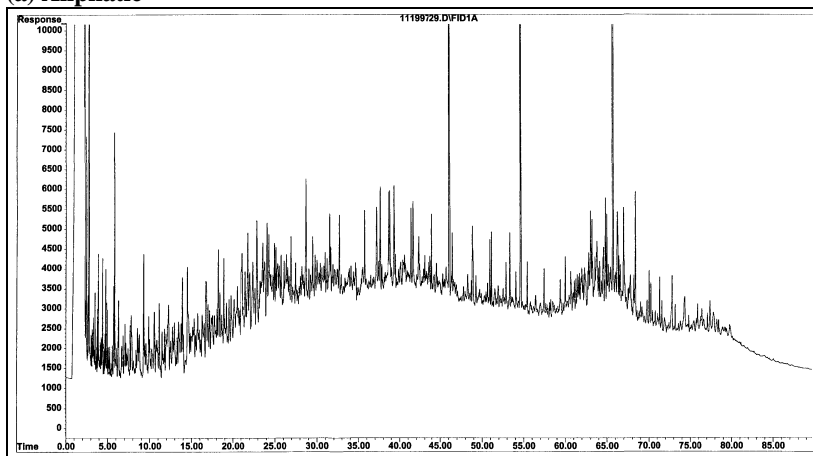
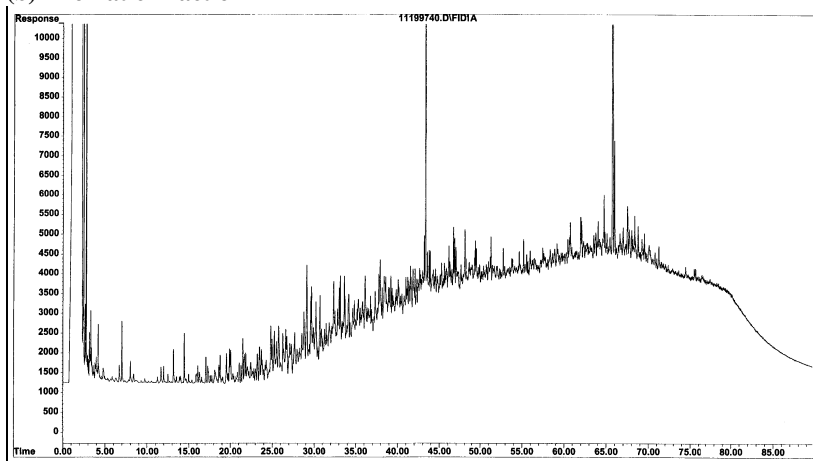
(a) Aliphatic**(b) Aromatic Fraction**

Figure 3. Aliphatic (a) and Aromatic (b) fractions of low API gravity crude oil.

Chromatographic Conditions

The original version of the TPHCWG analytical methodology did not include hydrocarbons greater than carbon number 28 (C_{28}). This is appropriate for most refined petroleum products such as gasoline and diesel. However, the concentration of hydrocarbons with carbon numbers greater than 28 (or even 35, the upper limit for the current TPHCWG analytical method) can be as high as 50 to 60% in some crude oils with low °API. Therefore, to conduct a better risk-

based analysis of sites where crude oil is present, it may be necessary to be able to detect hydrocarbons with carbon numbers greater than C_{35} . This can be done by modifying the gas chromatographic technique to quantify hydrocarbons up to C_{44} . (C_{44} is the upper limit for most gas chromatographs, and C_{44} is therefore the technical limit of the instrument. Hydrocarbons $>C_{44}$ may be present in crude oils as described in Chapter 4.) The chromatographic conditions necessary to do this are not routine in most environmental laboratories.

Because the TPHCWG analytical method is chromatography based, it is imperative that the chromatographic system not introduce large amounts of bias. In this analysis, the most common source of bias was found to be mass discrimination [3]. Mass discrimination is created when the chromatographic system, be it the chromatographic column or the detector, responds differently to different materials based on their relative mass. In the TPHCWG method, the use of a flame ionization detector (FID) ensures that discrimination does not occur at the detector end of the system. In general, the response of an FID is essentially the same for all hydrocarbons (on a weight basis). Saturated hydrocarbons and compounds containing heteroatoms, such as benzothiophene, have a slightly lower response than unsaturated, aromatic hydrocarbons because of the lower carbon to hydrogen and carbon to heteroatom ratio of these compounds.

Another source of mass discrimination can be created by injection port conditions if those conditions are preferential to a particular class or classes or compounds. In this case, the use of a narrow bore column [$0.25\text{ }\mu\text{m}$ inner-diameter (ID)] creates an injection port environment preferential to smaller, lower boiling point compounds. Larger, heavier, higher boiling point compounds may not enter the chromatographic column at the same rate and may be underestimated. The use of a wider bore column ($0.32\text{ }\mu\text{m}$ ID) and proper positioning of the column in the injection port can alleviate much of the mass discrimination. Mass discrimination of less than 20% between $n\text{-}C_{20}$ and $n\text{-}C_{40}$ can be easily maintained. When analyzing crude oils these performance criteria should replace that in the TPHCWG method comparing $n\text{-}C_{20}$ to $n\text{-}C_{28}$, as this range is more applicable to the analysis of crude oils. Special attention and maintenance must also be applied to the injection port.

The use of a wider bore column (e.g., $0.32\text{ }\mu\text{m}$ ID) can alleviate many mass discrimination problems, but can present new problems as well. The use of a wider bore column will reduce the separation of early eluting compounds, require a reduced temperature ramp rate, and result in longer analysis times. The recommended GC conditions for crude oil analysis are as follows:

Gas Chromatographic Conditions

Carrier Gas:	Helium
Carrier Gas Flow:	5 to 7 mL/Min.
Air Flow:	360 mL/Min.
Hydrogen Flow:	35 mL/Min.
Make-up Gas Flow:	30 mL/Min.
FID Temperature:	325°C
Injection Port Temperature:	275°C
GC Operation:	Splitless Mode
Straight Liner:	4 mm ID Packed With Glass Wool
Column Head Pressure:	12.0 psi @ 50°C
Linear Velocity:	Approximately 50 cm/sec
Oven Program:	Initial Temperature 10°C Hold for 5 Min. Ramp @ 4°C/Min. to 320°C Hold for 10 Min.
Column:	DB-5 30 m x -0.32 µm ID, 0.25 µm Film Thickness

Compound Specific Analyses Are Required

The TPHCWG has recommended using USEPA Method 8260 [1], a method specific to volatile organics, for accurately measuring benzene and toluene content of oils. The need to use USEPA 8260 to quantify volatiles was confirmed in this study. In addition, action levels for benzene and toluene are lower than can be achieved with the TPHCWG analytical method. The same applies to the measurement of individual target PAHs which should be determined using USEPA Method 8270 [1].

Summary

Analytical methods for determining the petroleum hydrocarbon content of soils should be performance based, with common data quality objectives for elements such as mass discrimination, mass balance, extraction efficiency, fractionation efficiency, and calibration. When sites have been impacted by crude oils, oil fractionation must be carefully determined and monitored, or risk-based screening levels may be biased.

Benzene and toluene concentrations should be determined by a method specific to volatile organics, such as USEPA Method 8260 [1]. These results can then be combined with the TPH determinations for risk analysis.

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Predicting the Fate and Transport of Hydrocarbons in Soil and Groundwater

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Introduction

Effective risk-based decision-making for chemicals that have been released to the environment requires a basic understanding of the fate and transport of the chemicals once released and how they interact with the different environmental media (such as soil, water, air, and biota) that they contact. This information is necessary in order to determine how people, or other receptors, might be exposed to the chemicals and what the associated risks might be.

Exploration and production (E&P) sites are usually concerned with spills of crude oils, condensates, or wastes that are associated with E&P activities. Accordingly, spills of individual chemicals are rarely of concern and instead, spills of hydrocarbon mixtures predominate. This is important to the evaluation of the fate and transport of chemicals at E&P sites because the presence of the hydrocarbon mixture will affect the solubility of any individual chemical and its movement in the environment.

When a chemical is introduced to soil, it can volatilize, sorb to soil particles, dissolve into the groundwater (or soil pore water), or remain in residual form. This partitioning of the chemical into other media is described by a set of simple mathematical equations. Movement of a chemical through different media depends on the unique physical and chemical properties of the individual chemical, the amount of the chemical in relation to the amount of total petroleum hydrocarbons (TPH) in the spill, and the properties of the media. In risk-based decision-making, this movement through the environment is typically modeled with a variety of fate and transport models. Some basic equations that can be used to estimate chemical transport will be presented in this chapter. Many of the fate and transport models typically used for risk evaluation are based on these equations.

The goal of this chapter is to provide an overview of the important fate and transport processes that affect petroleum spills in soil, and the estimation of risk from spills. The concept of partitioning when the chemical is part of a mixture

(Raoult's Law) is described, as are the potential implications of including Raoult's Law in fate and transport modeling of petroleum hydrocarbons.

Chemical Fate and Transport in Risk-Based Decision-Making

As described in Chapter 1, risk-based decision-making (RBDM) for environmental site management generally requires that a quantitative risk evaluation be performed. The risk evaluation process includes four technical elements, all of which are necessary for a complete evaluation of risk. The four elements are:

- Hazard Identification
- Exposure Assessment
- Toxicity (Dose-Response) Assessment
- Risk Characterization

Chemical fate and transport processes are integral to completing the exposure assessment. Figure 1 illustrates a simple conceptual site model (CSM) in which potential exposure pathways are shown for an oil production site. Workers may be exposed to surface soil, or to vapors from subsurface soil or groundwater, while off-site residents may be exposed to dissolved chemicals in their drinking water. Identifying exposure pathways is a critical component of risk-based decision-making and the CSM is a very useful tool for “visualizing” the exposure pathways that may exist at a particular site.

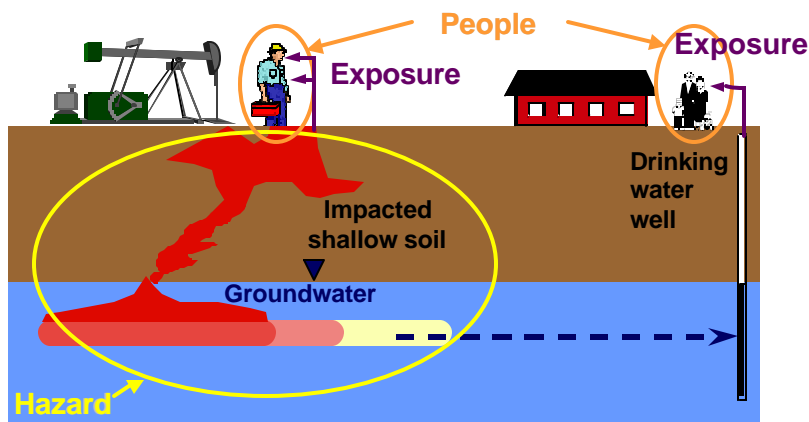


Figure 1. Example of a conceptual site model at an oil production site.

In order to quantitatively estimate the potential exposures that people might have, it is necessary to first know how much of the chemicals of concern may be present in the environment. This can be done either by actually measuring chemical levels in the different environmental media (soil, water, and/or air) or by estimating levels with mathematical models. Measurement of chemical concentrations is most often used for exposure pathways in which the receptor is directly exposed to the environmental medium of concern. Mathematical models are typically used to estimate the transfer of contaminants from the source of the chemical to the receptor for exposure pathways in which the receptor is indirectly exposed.

Many risk-based environmental management programs focus on potential human exposures to three environmental media: surface soil, subsurface soil, and groundwater [1,2,3]. Each of these media has more than one associated potential exposure pathway. This section describes the exposure pathways for each medium and indicates whether they are direct or indirect.

Surface Soil

Surface soil is usually defined as the soil at the ground surface that could directly contact a receptor. Most regulatory programs have defined the top 1-meter of soil to be “surface soil,” however some programs define this zone as the top 3 meters for residential scenarios. The potential exposure pathways that are associated with surface soil are:

- Ingestion of Soil
- Dermal Contact
- Inhalation of Volatile Emissions in Outdoor Air
- Inhalation of Dust Emissions in Outdoor Air

The first two exposure pathways are direct pathways and no modeling is required to estimate the concentrations of chemicals of potential concern that receptors may contact. The latter two pathways are indirect pathways in which the chemicals of potential concern originate in the impacted soil, but then are transferred to air as they volatilize. The concentrations of the chemicals of concern transferred from soil to breathing zone air must be estimated using mathematical fate and transport models.

Subsurface Soil

Subsurface soil is usually defined as the region directly beneath the surficial soil extending to just above the water table. A receptor is not likely to directly contact subsurface soil. However, soil in this unsaturated zone may act as a source of contamination to the ground surface via volatilization or to groundwater via leaching.

Three different exposure pathways may be of concern:

- Ingestion of Groundwater (From Leaching)
- Inhalation of Volatile Emissions in Outdoor Air
- Inhalation of Volatile Emissions in Indoor Air

All three pathways are indirect and, therefore, require the use of fate and transport models to estimate the concentrations of chemicals of potential concern to which receptors may be exposed.

Groundwater

There are usually three groundwater exposure pathways:

- Ingestion of Groundwater
- Inhalation of Volatile Emissions in Outdoor Air
- Inhalation of Volatile Emissions in Indoor Air

Ingestion of groundwater is a direct exposure pathway. The two volatilization pathways are indirect and therefore models are used to estimate volatilization from groundwater through the vadose zone.

In Tier 1 of most state risk-based corrective action (RBCA) programs, the groundwater risk-based screening levels (RBSLs), whether they are United States Environmental Protection Agency (USEPA) drinking water maximum contaminant levels (MCLs) or risk-derived numbers, are assumed to apply at the source of the contamination and are therefore required to be met everywhere in the aquifer. Some states, however allow the use of a “buffer zone,” which is some distance downgradient from the source, at which the groundwater targets must be met [4]. In the latter case, a transport model would be used to estimate the transport from the groundwater source area to the downgradient groundwater receptor exposure point.

Partitioning in the Source Area

The first step in modeling the fate and transport of a chemical in soil and groundwater is to describe the distribution of the chemical in the contaminant source region. The source region is defined in this chapter as the soil that contains the bulk of the contamination. For example, although the initial source of contamination may have been failed storage tanks, for risk assessment purposes the source is considered to be the contaminated soil surrounding the tanks that may serve as an ongoing source for chemical transport to a receptor.

The chemical distribution among the possible phases and locations in the soil pore spaces in the contaminant source region must be accurately described in

order to model the fate of the chemical in the environment. This is important because the chemical in the dissolved phase will move with the flow of groundwater (if in an aquifer) or move downwards with infiltration (if in the unsaturated zone). Similarly, only the chemicals in the vapor phase are assumed to be able to readily diffuse and flow with the soil vapor.

Partitioning describes the relative concentration of a chemical in two or more phases in contact with each other at equilibrium. The total mass of a chemical in soil is the sum of the mass in the vapor phase, dissolved phase, sorbed to soil, and any chemical in residual form (in the organic phase):

$$M_T = M_s + M_w + M_v + M_{org} \quad (1)$$

where:

M_T = Total mass of the chemical in the soil (kg)

M_s = Mass of the chemical sorbed to soil (including organic carbon) (kg)

M_w = Mass of the chemical dissolved in groundwater (kg)

M_v = Mass of the chemical in the vapor phase (kg)

M_{org} = Mass of the chemical in organic phase [as pure phase droplets or non-aqueous phase liquid (NAPL)] (kg)

Equation (1) would apply to the unsaturated zone where soil gas might be present. If the mass of the chemical is in groundwater only, the mass would be partitioned between the sorbed (sometimes called the solid phase), dissolved, and organic phases:

$$M_T = M_s + M_w + M_{org} \quad (2)$$

where the parameters are as defined above. In Equations (1) and (2), M_{org} can represent the mass of the pure form of the chemical, which occurs when a single chemical is spilled, or it can represent the mass of the chemical found in a separate-phase mixture, such as benzene in gasoline. The term, “separate-phase mixture” is often called “residual” by professionals in the fields of risk assessment and fate and transport. Used in this way, the term does not imply mobility, but instead merely indicates the presence of a free product phase in the soil. NAPL is also considered to be residual product.

Equilibrium Partitioning Equation

Equations (1) and (2) define the components of the total chemical mass in soil, however these equations don't show the relationships between the various phases. Every chemical has a specific affinity for the various phases that can be predicted with measured chemical properties and site-specific parameters. A

chemical with a higher affinity for water will have a higher solubility than a chemical with a lesser affinity for the water phase. Similarly, volatile compounds have a high affinity for the vapor phase. In order to predict the movement of the chemical in soil, the concentration in each phase must be known. In the unsaturated zone, the concentration of a chemical in the soil can be described as follows:

$$C_T = \theta_b C_s + \theta_w C_w + \theta_a C_v + \theta_{org} C_{org} \quad (3)$$

where:

- C_T = Total concentration of chemical in soil (mg chemical/g dry soil)
- C_s = Concentration of chemical sorbed to soil (mg chemical/g dry soil)
- C_w = Concentration of chemical in water (mg chemical/cm³ water)
- C_v = Concentration of chemical in vapor (mg chemical/cm³ vapor)
- C_{org} = Concentration of chemical in the organic phase (mg chemical/cm³ residual)
- θ_a = Air-filled porosity (cm³ air/cm³ dry soil)
- θ_w = Water-filled porosity (cm³ water/cm³ dry soil)
- θ_{org} = Porosity filled with residual phase liquid, either pure chemical (if a single chemical was spilled) or the NAPL mixture (cm³ residual/cm³ dry soil)
- θ_b = Soil bulk density (g dry soil/cm³ dry soil)

The total concentration in soil, C_T , is the concentration measured in the laboratory through the analysis of a soil sample. For petroleum hydrocarbons, the concentration in the organic phase, C_{org} , is the concentration of the individual chemical in the oil.

For spills containing no residual, Equation (3) is written [5]:

$$C_T = \theta_b C_s + \theta_w C_w + \theta_a C_v \quad (4)$$

Equation (4), often called the equilibrium partitioning equation, states that the total concentration in soil can be partitioned among the sorbed, dissolved, and vapor phases only; there is no residual present in the soil.

Many fate and transport models assume that the total concentration in soil can be partitioned into three phases using Equation (4) [5]. In other words, the models do not account for the separate oil phase. If the scenario being modeled contains a NAPL phase, then Equation (4) will overestimate the concentrations in each of the other three phases. Overestimation of the dissolved phase and soil vapor phase will result in overestimation of the rate of leaching and

volatilization. The following paragraphs describe how to determine whether the use of Equation (4) is appropriate for fate and transport modeling of a specific spill using the solubility of the chemical of interest.

Henry's Law Coefficient

Chemical partition coefficients are used to define the relationships between the various concentrations in each phase. Henry's Law coefficient, K_H , relates the dissolved phase concentration to the vapor phase concentration in the following manner:

$$K_H = \frac{C_v}{C_w} \quad (5)$$

where:

K_H = Henry's Law coefficient for chemical [(mg/L vapor)/(mg/L water)]

C_w = Concentration of chemical in water (mg chemical/cm³ water)

C_v = Concentration of chemical in vapor (mg chemical/cm³ vapor)

K_H has been measured for many chemicals and can be found in reference texts [6,7]. It can also be estimated from the chemical's vapor pressure [8]. Higher Henry's Law coefficients indicate chemicals with higher volatility. Values range from 0.23 to 0.33 for benzene, toluene, ethylbenzene and xylenes (BTEX) [7]. USEPA Region IX designates chemicals as being volatile if they have a molecular weight less than 200 g/mole (mol) and a Henry's Law coefficient of greater than 4.2E-4 (0.00042 units in dimensionless form) [9]. Table 1 shows Henry's Law coefficients and other important fate and transport parameters for BTEX.

Table 1. Chemical properties of BTEX [6,7].

Chemical Parameters	Molecular Weight (g/mol)	Vapor Pressure (mmHg)	Solubility (mg/L)	Henry's Law Coefficient -	K_{oc} (mL/g)
BTEX:					
Benzene	78.11	95	1770	0.227	6.6E+01
Ethylbenzene	106.17	9.6	169	0.328	2.0E+02
Toluene	92.14	28.2	530	0.276	1.4E+02
Xylenes	106.17	8.06	198	0.293	2.4E+02

The following equation is used to estimate the vapor phase concentration of a chemical in soil from the dissolved phase concentration [8]:

$$C_{vapor} \left(\frac{\mu g}{m^3} \right) = K_H \cdot C_{dissolved} \left(\frac{mg}{L} \right) \cdot \left(\frac{1000L}{m^3} \right) \cdot \left(\frac{1000\mu g}{mg} \right) \quad (6)$$

Note, in Equation (6), C_v is in units of $\mu g/m^3$ and $C_{dissolved}$ is in units of mg/L . Both of these units are commonly used in risk assessment. Often soil vapor concentrations are reported in units of parts per million-volume (ppmv); these units must be converted to concentration in terms of mass per volume before being used in risk assessment equations. For a gas at 25°C and 1 atmosphere (atm) of pressure the conversion is:

$$C_{vapor} \left[\frac{\mu g}{m^3} \right] = \frac{C_{ppmv} \cdot MW}{24.45} \left[\frac{10^6 \mu g}{g} \right] \left[\frac{10^3 L}{m^3} \right] \quad (7)$$

where:

C_{ppmv} = Concentration of chemical in vapor reported as ppmv

MW = Molecular weight of chemical (g/mol)

24.45 = Molar volume at 25°C and 1 atm (liter/mol)

$molar\ volume = \frac{RT}{P}$ to calculate at other temperatures

R = Universal gas constant = 8.21E-2 [(atm liter)/(mol Kelvin (K))]

T = Temperature of the gas (K) (K = °C + 273°)

P = Pressure of the gas (atm)

Soil-Water Sorption Coefficient

The soil-water sorption coefficient, K_d , describes the relationship between the concentration of the chemical sorbed to the soil to the concentration of the chemical dissolved in water. The basic Freundlich equation is [6]:

$$K_d = \frac{C_s}{C_w^n} \quad (8)$$

where:

K_d = Chemical-specific soil-water sorption coefficient [(mg chemical/g dry soil)/(mg chemical/cm³ water)]

C_w = Concentration of chemical in water (mg chemical/cm³ water)

C_s = Concentration of chemical sorbed to soil (mg chemical/g dry soil)

n = Freundlich exponent (dimensionless)

The sorption is usually assumed to be linear with respect to concentration in water (i.e., $n = 1$). The soil-water sorption coefficient depends on both chemical-specific and soil-specific properties. Most simple fate and transport models, (e.g. Jury model [5,10], VADSAT model [11]), for organic chemicals usually assume that K_d is equal to the product of the fraction of organic carbon, F_{oc} , and the organic carbon partition coefficient, K_{oc} , of the chemical:

$$K_d = F_{oc} \times K_{oc} \quad (9)$$

where:

F_{oc} = Fraction organic carbon in soil (g organic carbon/g soil)

K_{oc} = Chemical-specific organic carbon partition coefficient (mL/g)

The organic carbon partition coefficient can be found in many reference texts as well as USEPA documents for specific chemicals [7,8]. The fraction of organic carbon in soil is usually a site-specific value measured from a soil sample.

Equation (9) assumes that organic carbon is the sole predictor of chemical sorption in soil. Clay content, the presence of charged particles and the fact that organic carbon is somewhat difficult to measure, can cause the amount of chemical sorbed to soil to be underpredicted, and hence the amount in the other phases will be overpredicted. Lyman et al. [8] provides a discussion of the increased sorption expected due to mineral content in the soil and provides some equations for estimating the increased sorption. In some cases, it might be important to have a better estimate of K_d than that provided by Equation (9). If desired, K_d can be measured in the laboratory using soil gathered from the site.

Calculating Source Concentrations

Fate and transport models used for risk assessment usually begin with the estimation of the chemical concentration in groundwater. If the model is used to estimate volatile emissions, the vapor concentration is then estimated from the dissolved phase concentration using Henry's Law coefficient.

For soil spills not containing a residual phase, the equilibrium partitioning equation can be solved for the dissolved phase concentration by substituting Equations (5) and (8) into Equation (4):

$$C_w = \frac{?_b C_T}{?_b K_{oc} F_{oc} + ?_w + ?_a K_H} \quad (10)$$

Once C_w is calculated, the vapor phase concentration can be estimated:

$$C_v = C_w K_H \quad (11)$$

where the variables are as defined previously. Note, that the units of C_T and C_w are not the usual units reported in laboratory data. The conversions are as follows:

$$C_w \left[\frac{mg}{L} \right] = \frac{?_b \left[\frac{g}{cm^3} \right] C_T \left[\frac{mg}{kg} \right]}{?_b K_{oc} F_{oc} + ?_w + ?_a K_H} \left[\frac{kg}{1000 g} \right] \left[\frac{1000 cm^3}{L} \right] \quad (12)$$

In Equation (12), the soil concentration, C_T , can be taken from the unsaturated zone or below the water table. Equation (12) can be useful to predict the concentration of a chemical in groundwater from a measured soil concentration, however as written, it is not applicable for cases containing residual. If NAPL is present (and it can be difficult to detect visually), Equation (12) will overestimate the dissolved phase concentration. The presence of NAPL can be determined by considering the chemical's solubility in water. If the calculated dissolved phase concentration exceeds the chemical's solubility, then equation (12) is not applicable. Since Equation (12) assumes that the chemical can be partitioned into three phases (solid, dissolved, and vapor), then there must be a fourth phase present and Equation (3) should be used. It is very important to make sure that the fate and transport model includes the residual term (and thereby limits the dissolved phase and vapor phase concentrations) if it is likely that NAPL may be present in the soil.

Up until this point, the equations presented have been describing the behavior of a chemical partitioning in soil as if it were the only chemical present. In hydrocarbon mixtures, that is not the case and the chemical's solubility will be limited even further due to the presence of the overall TPH mixture. Raoult's Law predicts the effective solubility for chemicals that are in mixtures and accordingly, it should be used if the chemical being modeled is part of a mixture. The next section defines Raoult's Law.

Effect of Raoult's Law on Source Concentrations

In fate and transport screening models, the partition equations described earlier are usually applied in the source region to estimate the concentration of the chemical that is partitioning from the source to the vapor and/or dissolved phases. Fate and transport models typically consider one chemical at a time, and the partitioning of the chemical between water, soil vapor, and soil organic matter is calculated individually for each chemical. This is not an accurate approach for mixtures of petroleum hydrocarbons. When a chemical is part of a mixture, its partitioning behavior can change dramatically. This is especially

true for TPH, where each chemical usually represents a very small percentage of the overall mixture.

The accurate prediction of the concentration of an organic chemical contained in a mixture of many organic chemicals is essential to the assessment of potential risks. Accordingly, fate and transport equations used to examine petroleum hydrocarbons should include this “mixture effect.” In order to model organic chemicals as part of mixtures, the fate and transport equations require a minor modification. The required modification is to use Raoult’s Law to account for the chemical’s effective solubility in water.

Effect of Raoult’s Law on Dissolved Concentrations

The maximum dissolved concentration of a chemical in an organic mixture is a function of its pure compound solubility and the mole fraction of the chemical in the organic phase. Published pure compound solubility values are available for many compounds of concern and are listed in Table 1 for BTEX. When a chemical is part of an organic mixture, its solubility in water will be limited as follows:

$$C_{w\ max} = S_{eff} = x * S \quad (13)$$

where:

$C_{w\ max}$ = Maximum dissolved concentration of chemical in water (mg/L)
 x = Mole fraction of chemical in organic chemical mixture (mole chemical/mole oil)
 S = Solubility of pure chemical in water (mg/L)
 S_{eff} = Effective solubility of chemical in water (mg/L)

Equation (13) is known as Raoult’s Law and it is commonly used to predict the dissolved concentration of a chemical in water exposed to a hydrocarbon mixture [8]. For example, benzene with a pure compound solubility of 1,770 mg/L and a mole fraction of 0.001 in crude oil would have a maximum dissolved concentration of 1.77 mg/L. The maximum dissolved concentration, when calculated in this manner, is also called the effective solubility. The mole fraction is calculated from:

$$x = \frac{C_T MW_{TPH}}{MW_i C_{TPH}} \quad (14)$$

where:

C_{TPH} = Total concentration of total petroleum hydrocarbon in soil (mg/kg)
 C_T = Total concentration of individual chemical in soil (mg/kg)
 MW_{TPH} = Average molecular weight of hydrocarbon mixture (g/mol)

MW_i = Molecular weight of individual chemical (g/mol)

For chemicals with similar molecular weights, the mass fraction can be substituted for the mole fraction. For example, if benzene were reported in a soil sample at 100 mg/kg and the TPH concentration was reported to be 5,000 mg/kg, then the mass fraction would be $= 100/5,000$, or 0.02. Assuming the molecular weight of benzene and the TPH mixture were similar (perhaps the TPH is a light, refined product), the maximum dissolved phase concentration of benzene expected would be equal to $1,770 \text{ mg/L} \times 0.02 = 35.4 \text{ mg/L}$ (where benzene's solubility $= 1,770 \text{ mg/L}$).

Raoult's Law is valid for compounds that are liquids at room temperature. For solid compounds, such as the larger polycyclic aromatic hydrocarbons (PAHs), the "subcooled liquid solubility" is used in place of the pure chemical solubility (S) in Equation (13). These values are also available in the literature [12].

To confirm that Raoult's Law is appropriate for predicting the effective solubility of a chemical that is present in oil when the oil is in contact with water, 15 crude oils were analyzed for 43 aromatic compounds ranging from benzene through 5- and 6-ringed PAHs. The oil was then placed in contact with water and compounds present in the oil were allowed to partition into the water. The concentrations of the aromatic compounds in both the oil and water phases were determined. Figure 2 presents the data for all analytes in which the dissolved concentrations were above the analytical reporting limit of 5 ppb. Most of the results were at or below the dissolved concentration predicted by the application of Raoult's Law. This is evidence that Raoult's Law can be used to estimate the effective solubility of a chemical.

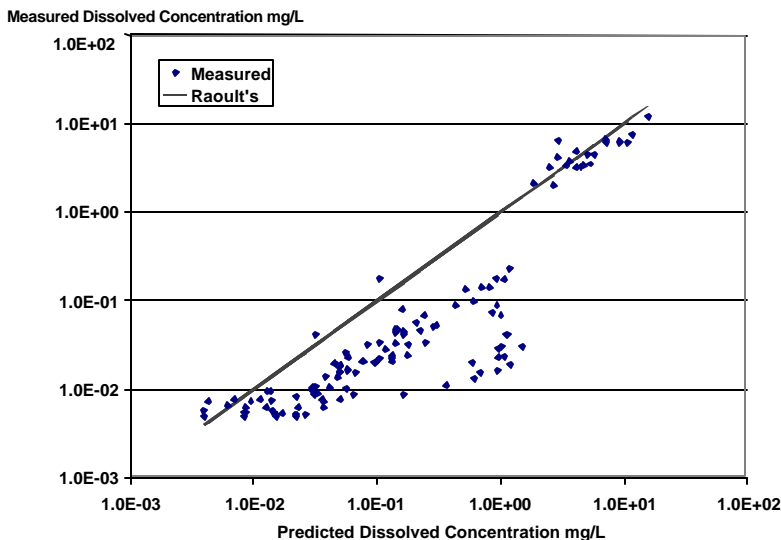


Figure 2. Measured dissolved concentrations of analytes are generally less than those predicted by Raoult's Law.

Equation (13) predicts the effective solubility of a chemical in water from the chemical's solubility, S , and mole fraction in the TPH, x . The concentration in water can also be predicted using the chemical's oil-water partition coefficient if known.

$$C_w = x \cdot S = \frac{C_o}{K_o} \quad (15)$$

where:

C_w = Dissolved phase concentration (mg/L)

C_o = Concentration of the individual chemical in the TPH (mg chemical/kg TPH)

K_o = Oil-water partition coefficient (L/kg)

x = Mole fraction of chemical in TPH (moles/mole)

Equation (15) can be used to calculate K_o for any organic phase if S and x are known. Since x is a mole fraction, an estimate of the average molecular weight of the organic phase is required.

$$K_o = \frac{MW_i}{S_i \cdot MW_{TPH}} (10^6 \text{ mg/kg}) \quad (16)$$

where:

MW_i = Molecular weight of the individual chemical (g/mole)

MW_{TPH} = Average molecular weight of the TPH (g/mole)

S = Solubility of the individual chemical (mg/L)

Based on the distribution of compounds in the following hydrocarbon products, typical values for MW_{TPH} in g/mole are:

Gasoline	100
Condensate	150
Diesel/Distillate	180
Crude Oil	200-250
Gas Oil	300

Effect of Raoult's Law on Vapor Concentrations

Raoult's Law is also applied when calculating vapor phase concentrations because the vapor phase concentrations are calculated from the dissolved phase concentration using Henry's Law coefficient [Equation (11)].

Soil vapor concentrations can also be calculated using the ideal gas law ($PV = nRT$), where the mass of the chemical and its molecular weight have been substituted for the number of moles, n :

$$C_v = \frac{x \cdot MW \cdot VP}{R \cdot T} \quad (17)$$

where:

C_v = Concentration of chemical in the vapor phase (g/m³)

VP = Vapor pressure of chemical (mmHg)

x = Mole fraction of chemical in liquid phase (underneath vapor) (-)

R = Universal gas constant, 0.06236 [(mmHg m³)/(mol K)]

T = Temperature in Kelvins (K) (293 K = 20°C)

Equations (17) and (13) both indicate that the soil vapor concentrations are limited by the presence of the TPH mixture because the mole fraction, x , will be less than one. No matter how much NAPL is present in the soil, the vapor and dissolved phase concentrations will not increase beyond their effective solubility and effective saturated vapor concentration.

Fate and Transport Processes

Fate and transport models are used to estimate concentrations in media other than the source media for indirect exposure pathways. The estimated cross-media concentrations can then be used to determine the exposure of a receptor to the chemical of concern, via the exposure pathways described earlier in this chapter.

The important transport processes addressed by these models include volatilization, leaching, advection (being carried with the air or water), and dispersion. For soil contaminants in the unsaturated zone, cross-media concentrations are estimated for the following transport processes:

- Leaching From Soil to Groundwater
- Volatilization From Soil to Outdoor Air
- Volatilization From Soil to Indoor Air

For contaminants in or on the groundwater, the transport processes that can be modeled include:

- Volatilization From Groundwater to Indoor Air
- Volatilization From Groundwater to Outdoor Air
- Transport in Groundwater to a Downgradient Location

The models used to estimate these transport processes and associated cleanup levels do not address the movement of NAPL as a separate phase (e.g., the vadose zone model SESOIL and the groundwater model AT123D [10]). Groundwater dispersion models are used to estimate concentrations in downgradient groundwater locations. These models are usually used in Tier 2 or Tier 3 risk analyses because the exposure point is located away from the source. Some state regulatory programs, however, do include groundwater transport to downgradient locations in Tier 1 [4].

The models commonly used for risk assessment tend to be screening models because they are usually based on assumptions like uniform soil properties and an unchanging groundwater flow field. Screening models are not applicable to engineering design problems, such as the design of extraction wells, or for complex hydrogeological flow regimes. Two examples of software that integrate screening level fate and transport codes with risk assessment are BP RISC and API DSS [11,10].

The next few sections of this chapter describe the key features usually found in screening models.

Air Models

If it is plausible that receptors could be exposed to soil emissions, then the estimation of volatilization from the contaminant source will be important. If the volatilization to the indoor air exposure pathway is being modeled, it often “drives” cleanup levels because it can generate very low cleanup concentrations due to deficiencies in the screening models. Screening models tend to overestimate concentrations in air because they ignore many potentially important processes impeding diffusion, they ignore biodegradation which can be a significant loss mechanism for hydrocarbons, and the models are often steady-state so they predict that the same exposure concentration will occur for the entire exposure duration. For carcinogens like benzene, risk is a function of total accumulated exposure and it is unlikely that a volatile emission exposure would remain constant over a long exposure duration.

Diffusion

In screening models, the volatilization rate is usually estimated using the following equation (from Fick’s Law) (e.g., Farmer’s emission model [10,13], groundwater emission model to indoor or outdoor air [11]):

$$E = D_{eff} \frac{(C_{vs} - C_{vf})}{L} \quad (18)$$

where:

E = Volatilization rate toward the structure (g/cm²/sec)

D_{eff} = Effective diffusion coefficient in soil (cm²/sec)

C_{vs} = Vapor concentration at the source (g/cm³)

C_{vf} = Vapor concentration in the soil just outside the building foundation or at ground surface (g/cm³)

L = Volatilization distance (cm)

The effective diffusion coefficient in soil, D_{eff} , is an extremely important input parameter to the volatilization models. The effective diffusion coefficient is calculated with the Millington-Quirk relationship and accounts for the tortuosity in the soil [11,13]:

$$D_{eff} = D_{air} \left(\frac{\tau_a^{10/3}}{\tau_T^2} \right) + D_{water} \frac{I}{K_H} \left(\frac{\tau_W^{10/3}}{\tau_T^2} \right) \quad (19)$$

where:

D_{air} = Molecular diffusion coefficient for chemical in air (cm²/sec)

D_{water} = Molecular diffusion coefficient for chemical in water (cm^2/sec)

T_T = Total porosity (cm^3/cm^3)

where the rest of the variables are as defined previously.

Diffusion coefficients in water are usually four orders of magnitude lower than diffusion coefficients in air, so the second term in Equation (19) only becomes important for cases with very low air content. Diffusion coefficients in air do not tend to vary over a wide range so the sensitive input variable becomes the air content of the soil. Because the models assume that the unsaturated zone is homogeneous, D_{eff} can greatly be overestimated. In reality, the presence of high water content soil layers will greatly impede the diffusion of volatile chemicals. It can be fairly simple to modify the screening models to include multiple soil horizons with varying soil moisture contents [11,13]. Figure 3 shows the sensitivity of calculated cleanup concentrations in subsurface soil with respect to changes in air-filled porosity. The rest of the parameter values were chosen from a “typical Tier 1” analysis.

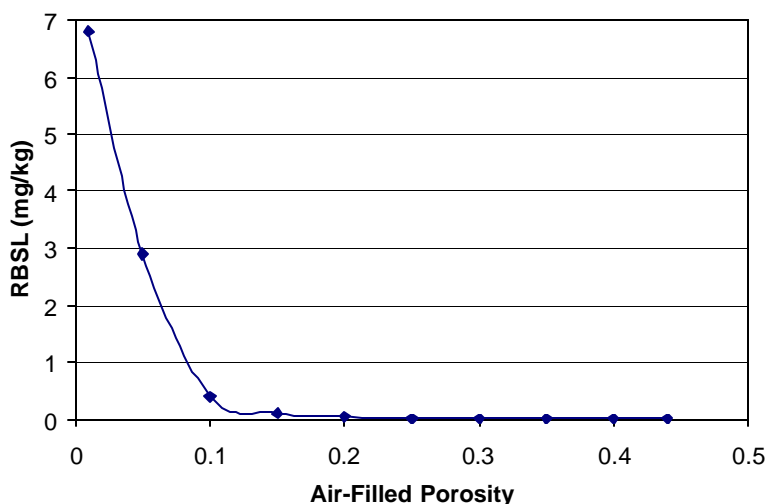


Figure 3. Sensitivity of subsurface soil RBSL for indoor air to changes in air-filled porosity.

When estimating concentrations in outdoor air, the vapor concentration in the soil at ground surface, C_{vf} , is assumed to equal zero (or is considered to be very small compared to the vapor concentration at the source). For the indoor air scenario, if pressure-driven flow is ignored, the vapor phase concentration in the soil just outside the building foundation is also assumed to equal zero.

Advection (or Pressure-Driven Flow)

Pressure-driven flow of the soil vapor may occur when a subsurface basement is underpressurized with respect to the soil gas surrounding it. This situation may arise due to wind loads on the building or heating systems operating in the basement. In Tier 1 analyses, pressure differentials are not considered. Some Tier 2 models include this term [11].

Mixing in Air

When using a screening model to estimate risk from volatile emissions, the breathing zone is usually assumed to be a “well-mixed box” that is ventilated by an air exchange rate. If the exposure pathway being considered is volatilization to outdoor air, it is assumed that the receptor is directly over the source, and the “box” is defined by the height of the breathing zone and the length of the source in the predominant direction of wind flow. The width of the “box” (perpendicular to the direction of wind flow) drops out of the equation. The breathing zone height is usually assumed to equal 2 m. For indoor air, the box is assumed to equal the volume of the building (for a house, it equals the volume of the house), and the ventilation rate is the rate at which the air in the building is exchanged with outdoor air.

Groundwater Models

The groundwater transport processes can be divided into those that occur in the unsaturated zone and those that affect transport in an aquifer. In a Tier 1 analysis, the only unsaturated zone “transport” that is considered is the leaching of the chemical of concern to the aquifer. In this case, the source in the unsaturated zone is assumed to be located at the water table so there is no opportunity for dispersion or degradation during transport to occur. Likewise, in the saturated zone, the only “transport” process that is considered is the mixing of the chemical in groundwater within a zone directly under the unsaturated zone. Transport of the chemical from this mixing zone to a point downgradient of the source is generally not considered in a Tier 1 analysis. As a result, the accurate partitioning of the chemical among the phases and locations in the soil pore spaces in the contaminant source region is essential for Tier 1 calculations.

Leaching From the Unsaturated Zone

Leaching from a source in the unsaturated zone is assumed to occur when water in the form of precipitation infiltrates through the source, dissolves chemicals and carries them to the water table. Screening models use the equilibrium partitioning equations to predict the dissolved phase concentration in the source region [2,10,11]. Usually the source is assumed to be uniform in concentration and box-shaped.

Under typical conditions, the amount of infiltration through the unsaturated zone will not equal the site's average precipitation because of evaporation, uptake by plants, and runoff. Many modelers assume a value in the range of 10 to 20% of the average precipitation as an infiltration rate. For example, if the average precipitation is 20 inches per year, a reasonable assumption for infiltration, or the amount of water that will reach the water table, is about 2 to 4 inches per year. The infiltration rate can be limited by the vertical hydraulic conductivity of the vadose zone soil. Consideration should also be given as to whether the source is underneath a paved area (thereby reducing infiltration) or in an area with artificially high recharge (such as a truck wash area). The American Petroleum Institute (API) has compiled a large database with recharge estimates from around the United States. A brief technical report is available from API summarizing the estimation of infiltration and the infiltration and recharge database [14].

The mass loading from the soil to groundwater is calculated from:

$$Q = C_w \cdot A \cdot I \left[\frac{L}{1000 \text{ cm}^3} \right] \quad (20)$$

where:

Q = Contaminant mass flux at the water table (mg/yr)

C_w = Dissolved phase concentration in leachate coming from source (mg/L)

I = Infiltration rate (cm/yr)

A = Cross-sectional area of source (cm^2)

Besides being used in Tier 1 equations [1,2], Equation (20) is used by many unsaturated zone models when they are linked with saturated zone models and used to estimate concentrations downgradient [10,11].

The average downward seepage velocity of the water in the unsaturated zone is calculated from [15]:

$$\bar{v} = \frac{I}{\theta_w} \quad (21)$$

where:

\bar{v} = Seepage velocity (cm/yr)

θ_w = Water-filled porosity (cm^3 water/ cm^3 soil)

In reality, the hydraulic conductivity in the unsaturated zone changes as the moisture content changes and water tends to move fast at first (a wetting front) and then most likely becomes steady. Equation (21) represents an average annual seepage velocity and is used by almost all simple analytical unsaturated zone models because the screening models are being used to estimate *long-term* loading to groundwater for purposes of calculating risk. This equation provides a handy “back-of-the-envelope” reality check for questions such as: “Could the dissolved phase have reached the water table?” and “Is the travel time to the water table so long that degradation will mineralize the chemical before it reaches the groundwater?”

Retardation (in Both Saturated and Unsaturated Zones)

Retardation describes a contaminant’s movement relative to the bulk movement of groundwater flow. The retardation factor, R , is estimated using the following equations for organic and inorganic chemicals:

$$R = 1 + \frac{F_{oc} K_{oc}}{q_w} \quad \text{for Organic Chemicals} \quad (22a)$$

$$R = 1 + \frac{K_d}{q_w} \quad \text{for Inorganic Chemicals} \quad (22b)$$

where:

F_{oc} = Fraction organic carbon in dry soil (g organic carbon/g soil)

K_{oc} = Organic carbon partition coefficient (mL/g or m³/kg)

K_d = Inorganic distribution coefficient (mL/g)

r_b = Soil bulk density of the saturated zone (g/cm³)

q_w = Water-filled porosity (cm³/cm³)

Retardation does not affect the results of screening models with constant source terms (steady-state models) that ignore degradation. It only becomes important when degradation is considered. This does not mean that the input parameters used in the retardation equation are unimportant because these variables are also used in the equilibrium partitioning equation, where they are very important.

Biodegradation

Biodegradation is usually assumed to be a first-order reaction in screening models, which means that it is assumed to be dependent only on time. In most models biodegradation is assumed to occur in the dissolved phase only, C_w (e.g., the groundwater models in the API DSS and BP RISC [10,11]). The sorbed phases and NAPL are assumed not to degrade. This means that biodegradation only begins as the contaminant migrates away from the source.

The biodegradation rate is probably one of the most sensitive input parameters for petroleum hydrocarbons, because the hydrocarbons that tend to be soluble, and therefore mobile, are also highly degradable [16,17]. Biodegradation is discussed in more detail in Chapter 11.

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Development of Reference Doses for Heavy Total Petroleum Hydrocarbon (TPH) Fractions

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Introduction

Over the last several years, a number of methods have been derived for evaluating potential human health risks associated with exposures to petroleum hydrocarbon mixtures. As described in previous chapters, the Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG) has conducted much of this work, focusing primarily on refined petroleum products, such as gasoline and diesel, which typically contain hydrocarbons below carbon number 35 (C_{35}). This chapter expands on the TPHCWG's work by taking into consideration potential risks associated with exposures to crude oils and exploration and production wastes which may contain heavy total petroleum hydrocarbon (TPH) fractions ($\geq C_{35}$). The United States Environmental Protection Agency (USEPA) and TPHCWG methodologies for developing reference doses (RfDs) and reference concentrations (RfCs) are described. RfDs are recommended for petroleum fractions $\geq C_{35}$ based on available toxicity studies.

USEPA Methodology for Determining RfDs and RfCs

In general, the USEPA's methods for determining RfDs and RfCs have remained relatively unchanged since the release of *Guidelines for Carcinogenic Risk Assessment* in 1986 [1]. Subsequent USEPA guidance which also discusses the development of RfDs include: *Risk Assessment Guidance for Superfund Volume 1 Human Health Evaluation* [2], *Reference Dose (RfD): Description and Use in Health Risk Assessments* [3], *Proposed Guidelines for Neurotoxicity Risk Assessment* [4], *Guidelines for Reproductive Toxicity Risk Assessment* [5], and *Guidelines for Developmental Toxicity Risk Assessment* [6].

Definition of Reference Dose and Reference Concentration

Health risks associated with non-cancer effects, such as organ damage, immunological effects, birth defects, and skin irritation, are assessed by comparing an estimated average exposure to an RfD or an RfC. RfDs and RfCs are not used to evaluate carcinogenic endpoints.

The RfD for any given chemical is “an estimate (with uncertainty spanning perhaps an order of magnitude) of a daily exposure to the human population (including sensitive subgroups) that is likely to be without appreciable risk of deleterious effects during a lifetime” [7]. Similar to the RfD, the RfC is also used to assess non-cancer effects. The RfC is “an estimate (with uncertainty spanning perhaps an order of magnitude) of continuous inhalation exposure to the human population (including sensitive subgroups) that is likely to be without appreciable risk of deleterious effects during a lifetime” [7]. Usually, exposures that are less than the RfD or RfC are not likely to be associated with health risks [2,8].

Derivation of RfDs and RfCs

Oral and dermal RfDs are calculated using the following equation:

$$\text{RfD} = \text{NOAEL or LOAEL} / (\text{UF}_1 \times \text{UF}_2 \dots \times \text{MF})$$

RfDs are typically expressed in units of milligram per kilogram per day (mg/kg/day).

The RfD is derived from a critical dose or concentration level usually described as a no-observed-adverse-effect level (NOAEL) or a lowest-observed-adverse-effect level (LOAEL) identified from toxicity studies in scientific literature. A suitable uncertainty factor (UF) is applied to the NOAEL or LOAEL to reflect differences between the study conditions and the human exposure to which the reference value will be applied. In addition, a modifying factor (MF) may be applied which reflects the completeness of the supporting scientific database.

Inhalation RfCs are derived from essentially the same equation as that used to develop RfDs. However, the NOAEL is converted into units of milligram per cubic meter (mg/m³) based on the exposure level. Thus, the units for inhalation RfCs are expressed in mg/m³.

Selection of Appropriate Data for Development of RfDs and RfCs

The first step to develop an RfD or an RfC is to identify a critical study and determine the NOAEL. The NOAEL is the highest dose at which no adverse effects are observed. If the NOAEL is not available, then a LOAEL can be used. However, use of the LOAEL adds an additional uncertainty factor into development of the RfD or RfC. NOAELs and LOAELs are usually based on laboratory dose-response experiments on animals that are exposed to relatively high doses. To develop an oral RfD the most appropriate source of the NOAEL or LOAEL is a chronic oral study. If there are no chronic oral data available, then subchronic oral data can be used instead. Again this adds another level of uncertainty into the derivation of the RfD. In some cases, chronic and subchronic inhalation studies can be used to develop oral RfDs when no oral

data are available. Most other toxicity data (i.e., dermal, acute, or genotoxic) are not recommended for use in the development of RfDs. Oral studies are not used in the development of inhalation RfCs.

Uncertainty and Modifying Factors

In general, UFs are applied in multiples of 10 and can range from 1 to 10,000. Descriptions of some UFs are as follows:

- Use a 10-fold factor when extrapolating from valid experimental results in studies using prolonged exposure to average healthy humans. This factor is intended to account for the variation in sensitivity among the members of the human population and is referenced by USEPA as “10H.”
- Use an additional 10-fold factor when extrapolating from valid results of long-term animal studies when results of human studies are either not available or inadequate. This factor accounts for the uncertainty involved in extrapolating from animal data to humans and is referenced by USEPA as “10A.”
- Use an additional 10-fold factor when extrapolating from less than chronic (lifetime exposure) results on experimental animals when there are no useful long-term human data. This factor is intended to account for the uncertainty involved in extrapolating from less than chronic NOAELs to chronic NOAELs and is referenced by USEPA as “10S.”
- Use an additional 10-fold factor when deriving the RfD or RfC from a LOAEL instead of a NOAEL. This factor is intended to account for the uncertainty involved in extrapolating from LOAELs to NOAELs and is referenced by USEPA as “10L.”

The MF is an additional safety factor that is occasionally applied based on the strength of the database and professional judgment. Typically, MFs range from 1 to 10 and are based on a subjective evaluation of the adequacy of the toxicity data.

TPHCWG Methodology for Determining RfDs and RfCs

The general risk assessment methodology selected by the TPHCWG for evaluating petroleum hydrocarbon mixtures is a combined indicator/surrogate approach, which is consistent with USEPA methodology [1]. Indicators are referred to as the single compounds within petroleum mixtures that are known to be toxic. In the United States, they are typically evaluated and regulated individually at either the federal or state level. Carcinogenic indicators are

usually evaluated first because their presence (even in relatively low concentrations) may drive a site cleanup, due to their greater relative toxicity. A surrogate approach is used for the non-carcinogenic mixtures (petroleum fractions) which represent the mass of petroleum remaining after evaluating the indicators. In order to support this type of risk assessment approach, toxicity criteria, such as RfDs and RfCs, must be developed for each of the petroleum fractions.

The Massachusetts Department of Environmental Protection (MADEP) appears to have developed the first fractional approach to evaluating the risk of TPH [9]. In 1995, British Columbia Environment (BCE) modified the MADEP approach to include fate and transport of fractions and to be specific for ecological receptors of concern in the province [10].

The TPHCWG evaluated subchronic, chronic, reproductive, developmental, immunotoxicity, and neurotoxicity data on petroleum fractions available in scientific literature. The USEPA's NOAEL-based methodology to develop oral and dermal RfDs was followed, and route-to-route extrapolation was minimized, i.e., oral studies were used for oral criteria, wherever possible. The development of benchmark doses was considered as an alternative approach to using NOAELs. However, the methodology for deriving a benchmark dose was believed to be less established and more controversial [11].

The fraction-specific oral RfDs and inhalation RfCs recommended by the TPHCWG are listed in Table 1. Petroleum fractions are based on environmental fate and transport characteristics of the constituents within a given carbon range rather than differences in toxicity. The methodology used to select the equivalent carbon ranges is described in the TPHCWG's Volume 3 *Selection of Representative Total Petroleum Hydrocarbon (TPH) Fractions Based on Fate and Transport Considerations* [12].

Table 1. Preliminary TPHCWG toxicology fraction-specific oral RfDs and inhalation RfCs.

Carbon Range¹	Aromatic Oral RfD (mg/kg/Day)	Aromatic Inhalation RfC (mg/m³)	Critical Effect	Aliphatic Oral RfD (mg/kg/Day)	Aliphatic Inhalation RfC (mg/m³)	Critical Effect
Aliphatic C ₅ -C ₆ C _{>6} -C ₈ Aromatic C _{>7} -C ₈	0.2	0.4	Hepatotoxicity Nephrotoxicity	5.0	18.4	Neurotoxicity
C _{>8} -C ₁₀ C _{>10} -C ₁₂ C _{>12} -C ₁₆	0.04	0.2	Decreased Body Weight	0.1	1.0	Hepatic and Hematological Changes
C _{>16} -C ₂₁ C _{>21} -C ₃₅	0.03 ²	NA	Nephrotoxicity	2.0	NA	Hepatic (Foreign Body Reaction) Granuloma

1) Carbon range: equivalent carbon range [12].

2) This is the pyrene (C₁₆) value.

RfD = Reference Dose.

RfC = Reference Concentration.

NA = Not available.

As shown in Table 1, the TPHCWG developed oral RfDs for aliphatic and aromatic petroleum fractions ranging from C₅-C₃₅ and inhalation RfCs for the aliphatic and aromatic fractions from C₅-C₁₆ [13]. Due to the limitations of the experimental design of available toxicity studies, the TPHCWG did not develop dermal RfDs for the petroleum fractions in these carbon ranges.

Based on both observed toxicity and uncertainty associated with the available studies, the RfDs for the aromatic fractions are at least an order of magnitude lower than those for the aliphatic fractions. Although more toxicity data were available for the aliphatic fractions, the data available for aromatic fractions indicate greater toxicity. In addition, greater uncertainty was factored into the development of the aromatic fraction RfDs than into the aliphatic fraction RfDs because toxicity data were limited on the aromatic fractions from C₉-C₁₆ and from C₁₇-C₃₅.

For the C₁₇-C₃₅ aromatic fraction, the TPHCWG assigned an oral RfD of 0.03 mg/kg-day based on the indicator compound pyrene with a carbon number of 16 (C₁₆). This was necessary because no other toxicity data were available for any aromatic compound with a higher carbon number, with the exception of carcinogenicity data on polycyclic aromatic hydrocarbons (PAHs). The aromatic fraction C₁₇-C₃₅ contains PAHs that are normally considered to be indicator compounds for risk assessment purposes.

Toxicity Assessment of Petroleum Hydrocarbons Above C₃₅

Petroleum hydrocarbons greater than C₃₅ are not normally addressed from a risk perspective in the United States. However, the toxicity of this heavier petroleum fraction may need to be assessed for many types of crude oils or heavy refined products (e.g., Bunker C). Therefore, the toxicity data for petroleum streams with high boiling ranges were evaluated. A few of these toxicity studies were useful for developing RfDs. These studies include two 28-day dermal toxicity studies of two vacuum residuum samples and several 90-day oral studies on white mineral oils and microcrystalline waxes (C₂₂-C₈₀). No toxicity data were available to assess the aromatic hydrocarbon fraction C₃₅-C₄₄. Therefore, the RfD of pyrene (C₁₆) must be used for this fraction, as the TPHCWG did for C₁₇-C₃₅ aromatics.

White Mineral Oils and Microcrystalline Waxes – 90-Day Oral Studies

Toxicity data on aliphatic hydrocarbon fractions (high molecular weight white mineral oils) were available for carbon numbers from C₃₅ to approximately C₄₄. These white mineral oils decrease in toxicity by an order of magnitude as compared to lighter molecular weight white mineral oils (C₁₇-C₃₅). The reason for this decrease in toxicity was believed to be the reduced bioavailability of these heavier compounds. Based on a 90-day oral study with white mineral oils, an oral RfD of 20 mg/kg/day was developed for the aliphatic fraction containing C₃₅-C₄₄ [13].

The same RfD for C₃₅-C₄₄ can be extended to include aliphatics up to C₈₀ based on 90-day oral studies on microcrystalline waxes [14]. These waxes are derived from the highest boiling petroleum fractions and have viscosities ranging from 10-30 centistokes at 100°C. These waxes are highly refined, saturated, aliphatic hydrocarbon mixtures with <1% aromatics. Two microcrystalline waxes were included in a 90-day oral toxicity study in Fischer 344 rats. One wax was a high sulfur wax (HSW) containing an average carbon distribution of C₂₀-C₇₄. The other was a high melting point wax (HMPW) with an average carbon distribution of C₂₂-C₈₀. In this study, rats were fed diets containing either HSW or HMPW at concentrations of 2, 20, 200, or 2,000 mg/kg/day. HSW and HMPW did not produce adverse toxic effects as evidenced by organ weights, hematology, clinical chemistry, or histopathology [14].

The NOAEL for this rat study is 2,000 mg/kg/day. Using an UF of ~100 (3 for animal-to-human extrapolation, 10 for subchronic-to-chronic extrapolation, and 3 for individual susceptibility), an oral RfD of 20 mg/kg/day was developed. This UF was also used by the TPHCWG for white mineral oils [13].

In addition, the amount of hydrocarbons in the liver following oral exposure to these HSW and HMPW was evaluated. No hydrocarbons were deposited in the livers of animals fed microcrystalline waxes. Moreover, it was concluded that no hydrocarbons with carbon numbers $C_{\geq 35}$ (boiling point 491°C) are passing the intestinal membranes [15]. Therefore, applying an oral RfD of 20 mg/kg/day to the $C_{\geq 35}$ fraction is extremely conservative.

Vacuum Residuum - 28-Day Dermal Studies

The American Petroleum Institute [16,17] conducted two 28-day dermal studies on vacuum residuum in rabbits. Vacuum residuum is defined as the residue obtained from the vacuum distillation of crude oil after all other fractions have been recovered, usually containing a mixture of hydrocarbon types $>C_{44}$. The vacuum residuum fraction of a crude oil is comprised of very large molecules (those that boil above approximately 600°C) that are not well characterized as to their compositional make-up, but it is known to contain a mixture of aliphatics, aromatics, metals, and asphaltenes. This fraction is also enriched in heteroatoms (nitrogen, sulfur, and oxygen containing compounds) [18]. From a mobility perspective, the high molecular weight hydrocarbons $>C_{44}$ will not move significantly from the area of release via groundwater. Therefore, they will remain together as a mixture in the environment. In addition, these materials are not volatile so exposure by inhalation would not be significant. Therefore, it is appropriate to develop a RfD for the combined aromatic and aliphatic fraction $>C_{44}$. The risk posed by these materials would be limited to direct contact by oral or dermal routes of exposure.

Rabbits were exposed to vacuum residuum at concentrations of 200, 1,000, and 2,000 mg/kg, three times a week for 4 weeks. Rabbits exposed to 2,000 mg/kg displayed decreased food intake and skin lesions. When compared to controls, no adverse systemic effects were noted in response to vacuum residuum exposure. The NOAEL for these studies was 2,000 mg/kg. A preliminary dermal RfD of 0.8 mg/kg/day was developed with the understanding that these are only 28-day studies.

The preliminary dermal RfD of 0.8 mg/kg/day was developed by converting 2,000 mg/kg to units of mg/kg/day. To convert to units of mg/kg/day, the mg/kg/week dose (2,000 mg/kg x 3 times a week) was divided by 7 to yield a NOAEL of 800 mg/kg/day. In addition, an UF of 1,000 was used (a factor of 10 for each of the following: animal-to-human extrapolation, individual susceptibility, and subchronic-to-chronic extrapolation).

These vacuum residuum studies do not lend themselves to development of an oral RfD for $>C_{44}$. Because it is generally accepted that oral bioavailability is greater than dermal bioavailability, an oral RfD would probably be lower than the derived dermal RfD. Based on the differences in bioavailability, it may be

reasonable to assume an UF of 10 for dermal-to-oral bioavailability, suggesting an oral RfD of 0.08 mg/kg/day could be developed for petroleum fractions $C_{\geq 35}$. This oral RfD is greater than the oral RfD of 0.03 mg/kg/day assigned by the TPHCWG for aromatic fractions containing C_{17} - C_{35} .

Summary

Literature searches for toxicity data on heavy petroleum hydrocarbons (i.e., $C_{\geq 35}$) were conducted and USEPA approved methods for developing RfDs were followed. This work followed the same general procedures used previously by the TPHCWG for developing petroleum fraction-specific RfDs. RfDs were developed for separate aromatic and aliphatic fractions containing hydrocarbons from C_{35} - C_{44} . For the $>C_{44}$ fraction, one RfD was developed for the combined aliphatic and aromatic fraction, known as the vacuum residuum fraction.

For the aliphatic hydrocarbon fraction C_{35} - C_{44} , an oral RfD of 20 mg/kg/day was developed from studies of high molecular weight white oils and microcrystalline waxes. For the aromatic hydrocarbon fraction C_{35} - C_{44} , there were no data available that could be used to develop either a dermal or an oral RfD. Lacking any data for the aromatic hydrocarbon fraction C_{35} - C_{44} , an RfD of 0.03 mg/kg/day could be assigned, based on the RfD for pyrene, a C_{16} component of petroleum. The TPHCWG used this approach for the C_{17} - C_{35} aromatic fraction.

Based on negligible mobility, there is no scientific advantage to separating aromatic from aliphatic hydrocarbon fractions above C_{44} . A preliminary *dermal* RfD of 0.8 mg/kg/day can be derived for a single hydrocarbon fraction ($>C_{44}$). This dermal RfD is based on dermal studies on vacuum residuum, which contains aliphatic and aromatic compounds as well as resins and asphaltenes. It is believed that using vacuum residuum as a surrogate for this fraction of crude oil is conservative.

There were no oral toxicity studies found that could serve as the basis for an oral RfD. It might be possible to develop an oral RfD based on the dermal data from the vacuum residuum studies. However, the USEPA has not traditionally accepted oral RfDs based on dermal data. If an oral RfD is developed based on the dermal data from the vacuum residuum studies, then it may be reasonable to assume an UF of 10 for dermal-to-oral bioavailability. This would suggest that an oral RfD of 0.08 mg/kg/day could be developed for the single petroleum fraction $>C_{44}$. However, since this approach is not recommended by the USEPA, the Petroleum Environmental Research Forum (PERF) 97-08 project team chose to use a very conservative approach by applying an oral RfD of 0.03 mg/kg/day (based on the oral RfD of pyrene) and a dermal RfD of 0.8 mg/kg/day for the $>C_{44}$ fraction.

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Developing Total Petroleum Hydrocarbon Risk-Based Screening Levels for Sites Impacted by Crude Oils and Gas Condensates

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Introduction

A review of upstream regulations summarized in Chapter 2 indicated that there is a need to develop a risk-based approach for establishing total petroleum hydrocarbon (TPH) regulatory limits, particularly for crude oils, condensates, and their associated wastes at exploration and production (E&P) sites. To accomplish this goal, a technically sound approach for determining the potential risk of crude oils and condensates based on their composition must first be developed, and then this risk-based approach to assessment and management must be accepted by upstream environmental regulators. TPH risk-based screening levels (RBSLs) address the risk of adverse non-cancer human health effects associated with the bulk of the hydrocarbons in complex petroleum mixtures. TPH RBSLs are first determined for each TPH equivalent carbon fraction and then a single TPH RBSL is calculated based on the specific mixture or oil composition, taking into account all of the individual TPH fractions. This chapter will describe the TPH RBSLs developed for use in the United States based on the composition of 70 crude oils and 14 condensates.

Developing TPH RBSLs

Procedures for deriving TPH RBSLs were developed by incorporating a modified Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG) fractionation scheme, (see Chapters 4 and 5), fate and transport properties, (see Chapter 4), and toxicity criteria developed for the equivalent carbon number TPH fractions, (see Chapter 7), into the American Society for Testing and Materials (ASTM) risk-based corrective action framework [1]. The potential exposure scenario for which TPH RBSLs were developed was that of a spill of crude oil or condensate at an oil or gas production site. Figure 1 illustrates the exposure scenario.

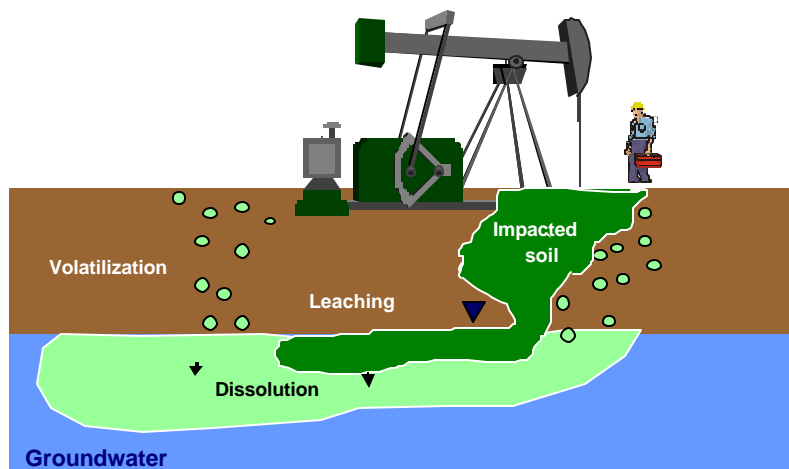


Figure 1. Potential exposure pathways for current production site workers .

Under current conditions at the site, workers may be exposed to contaminated surface soil, or to vapors from subsurface soil or groundwater. In the future, the land could be redeveloped for some other type of commercial or industrial use, or it could be redeveloped for recreational or residential purposes. In these cases, the future receptors could be exposed through the same exposure pathways that currently apply to workers. Since most E&P sites are located in remote areas, the most reasonably expected future land uses are generally non-residential, and therefore the primary focus of the TPH RBSL development will be on the non-residential case. However, it is possible that some sites will be redeveloped for residential purposes, and therefore TPH RBSLs will also be derived for residents.

Characteristics of Oils Used to Develop RBSLs

The 70 crude oils used to develop RBSLs were selected to cover a wide range of American Petroleum Institute (API) gravity values and geographical locations. The API gravity for these crude oils ranges from 8.8° to 46.4° and they are representative of all crude oil types produced globally. More details on these oils are presented in Chapter 4. Therefore, this data set can be used to set Tier 1 TPH RBSLs for all crude oils. The condensate data set is smaller (14 samples), but it does represent a wide API gravity range (46° to 70°).

RBSL Calculation Procedures

The RBSL calculations followed the general approaches and algorithms used by the TPHCWG and in the ASTM “Standard Guide for Risk-Based Corrective Action applied at Petroleum Release Sites” [1]. The variables and the specific

values used to estimate exposure are presented in Tables 1 and 2. These are also generally consistent with those presented in the ASTM standard; however, a few modifications have been made to better reflect current risk assessment practices in the United States. Recent scientific data and regulatory guidance suggest that revision of some of the default values originally presented in the ASTM standard is appropriate. Two variables, the relative dermal absorption factor (RAFd) and the skin adherence factor (M), were updated to better reflect more current state and United States Environmental Protection Agency (USEPA) default values [2,3,4,5,6,7,8,9,10]. In the absence of chemical-specific information, an RAFd of 0.1 and an M of 0.2 mg/cm² were assumed for all organic chemicals. These values are consistent with current United States federal and state guidance.

Table 1. Summary of dermal absorption factors and skin adherence values used by selected regulatory agencies.

Chemical	Relative Dermal Absorption Factor (RAFd)
Organics	0.10 [2,3,5,8] 0.10 (for Non-PAH) [4]
Polyaromatic Hydrocarbons	0.15 [4] 0.20 [9] 0.13 [2,3]
Volatile Organic Compounds	0.10 [6]
Semi-Volatile Organic Compounds	0.10 [10]
	<hr/> Soil to Skin Adherence (M), mg/cm ² <hr/>
All Chemicals	0.2 [5,7,8,10] 1.0 [4] 0.08 for Adults and 0.3 for Children [2] 0.10 for Adults and 0.2 for Children [3]

Some previously published residential RBSLs (based on United States exposure parameters) did not include potential exposures during childhood in the example calculations [1,11]. Residential RBSLs should include the potentially higher overall exposure levels that people may experience during childhood. Exposure parameters for residential sites presented in Table 2 include childhood specific ingestion and dermal exposure parameters. These parameters are consistent with current risk assessment practice and with United States federal and state regulatory guidance [8,12,13].

Table 2. Exposure factors used in calculating RBSLs [8,10,12,13].

Definition	Units	Symbol	Residential Value	Non-Residential Value
Ingestion Rate, Soil	mg/day	IR _{soil}	191	50
Inhalation Rate (Outdoor)	m ³ /day	IR _{soil}	8.3	31
Soil to Skin Adherence	mg/cm ²	M	0.2	0.2
Skin Surface Area	cm ²	SA	2800	3300
Body Weight	kg	BW	15	70
Exposure Time	hours/day	ET	24	8
Exposure Frequency	days/yr	EF	350	250
Exposure Duration	years	ED	6	25
Averaging Time (Non-carcinogens)	years	AT	6	25

The commercial exposure scenario, as defined in the ASTM guidance, was reevaluated as part of this analysis and was found to be protective of other non-residential exposure scenarios that may be more directly applicable to E&P operations. For example, the ASTM commercial scenario was found to be adequately protective for oil field workers and recreational land use. RBSLs derived for adults in a commercial setting, as defined by ASTM, were equal to or lower than those derived for adult oil field workers and adults and children in a recreational setting. Based on interviews with E&P environmental health and safety professionals, oil field workers were assumed to spend 30-40% of an average workday in a truck traveling within or between E&P sites and 60-70% of the day checking flows or volumes and performing maintenance activities. The primary exposure route for these workers was assumed to be inhalation of volatile materials and there was assumed to be little or no direct contact with contaminated site soils, groundwater or surface water. Recreational receptors were assumed to be on site for a full 2-week vacation period every year for 30 years or were assumed to be on site 4 hours per day, 2 days per week, 9 months per year for 30 years. Based on these findings, the commercial exposure scenario is referred to as a non-residential (commercial and recreational) scenario in this analysis.

A single, composite TPH RBSL was calculated for each of the 70 crude oils and 14 condensates. This composite RBSL was calculated by summing the Hazard Quotients (HQs) for the 13 equivalent carbon number fractions. The Hazard Quotient for any given fraction is the ratio of the level of exposure of that fraction over a specified time period to the reference dose assigned to that fraction. The sum of the individual Hazard Quotients is called the Hazard Index (HI) and it is set equal to one. The HQ for each equivalent carbon number fraction was calculated by taking the weight of the fraction multiplied by the total TPH (mg/kg) and dividing by the RBSL of the fraction.

RBSLs for Crude Oils and Selected Products

Residential and non-residential RBSLs were developed for 70 crude oils using the parameters described above. Additionally, five products made from crude oil (gasoline, baby oil, mineral oil, diesel, and Vaseline®) were analyzed. The modified TPHCWG fractions were determined for all these petroleum materials and the data were used to calculate RBSLs. The modifications to the fractions take into consideration those hydrocarbons that cover the entire range of hydrocarbons that may be present in crude oil.

RBSLs were developed for both residential and non-residential land uses. The following discussion focuses on the non-residential case, because it is the most likely land use for E&P sites under current and reasonably expected future conditions. Residential RBSLs are also presented; however, due to the overall higher exposure potential at residential sites, and the potential for additional exposure pathways to be present, it would generally be prudent to consider collecting at least some site-specific information prior to applying Tier 1 RBSLs to residential sites.

The RBSLs calculated for some products refined from crude oil (gasoline, diesel, mineral oil, baby oil, and Vaseline®) are shown in Table 3. All RBSLs are in units of mg-TPH per kg-soil (mg/kg). The exposure pathway with the lowest TPH RBSLs for all of the products involves direct human contact with surface soil, as long as benzene is considered as a separate indicator compound and is not included in the TPH RBSL. See Chapter 11 for an evaluation of benzene risk.

The non-residential surface soil RBSL for baby oil is 269,000 mg/kg (or 26.9%), for mineral oil is 313,000 mg/kg (or 31.3%), and for Vaseline® the value is 333,000 mg/kg (or 33.3%). The calculated RBSLs for baby oil, mineral oil and Vaseline® validate that the assumptions used for the exposure pathways and for the toxicity and fate parameters are extremely conservative, since these products are known to be safe for human contact and/or ingestion. Baby oil, mineral oil and Vaseline® contain only high molecular weight aliphatic compounds and no aromatic hydrocarbons (the more toxic and water soluble hydrocarbons), thus they should have high RBSL values. In contrast, gasoline, which is composed of hydrocarbons mainly ranging from C₅ to C₁₀ has the lowest RBSL. However, benzene will drive the risk at gasoline spill sites, since gasoline products may contain several percent benzene. Diesel which contains approximately 30% aromatics, and has a molecular weight range of ~C₁₀ to C₂₂, has a RBSL of 42,000 mg/kg.

Table 3. TPH risk-based screening levels for five refined petroleum products.

	Non-Residential Scenario		
	Leaching to GW (mg/kg)	Outdoor Vaporization (mg/kg)	Surficial Soils (mg/kg)
Gasoline	RES*	RES	30,000
Diesel	RES	RES	42,000
Baby Oil	RES	RES	269,000
Mineral Oil	RES	RES	313,000
Vaseline ®	RES	RES	333,000

*RES or residual saturation indicates that the oil does not pose a significant risk to human health even when present as residual material in soil.

Non-residential TPH RBSLs for each of the 70 crude oils analyzed as part of this study are plotted versus their API gravity in Figure 2. These RBSLs are based on direct human contact with contaminated surface soils. Leaching to groundwater and volatilization to outdoor air are not exposure pathways of concern for crude oils because most of the equivalent carbon fractions found in crude oils are either not soluble or volatile enough to cause a concern.

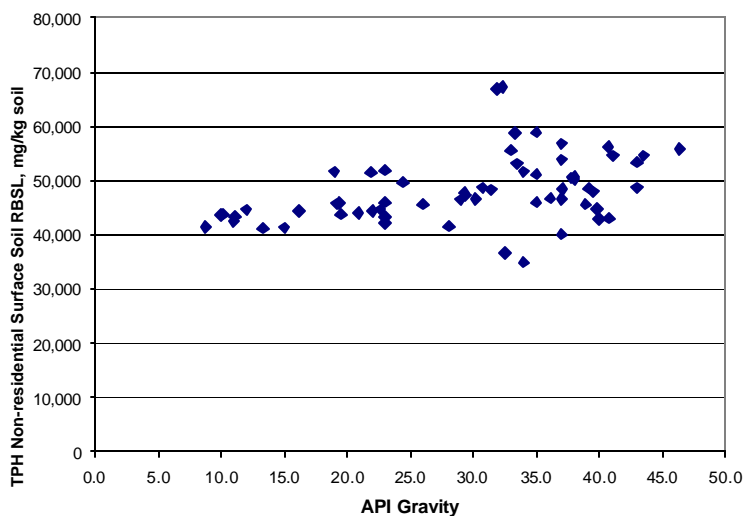


Figure 2. Non-residential surface soil TPH RBSLs calculated for 62 crude oils from around the world plotted by their API gravity. (API gravity data are not available for 8 of the 70 crude oils analyzed.)

The non-residential surficial soil RBSLs are greater than or equal to 35,000 mg-TPH/kg-soil as shown in Figure 2. The highest RBSLs were 67,300 and 67,900 mg/kg, which were obtained for two very waxy crude oils containing high amounts of the larger molecular weight aliphatic hydrocarbons (these hydrocarbons are the least toxic). While there does not seem to be a good correlation between calculated RBSLs and API gravity, the data are plotted in this manner to illustrate the range of RBSLs obtained and the diversity of crude oil types analyzed.

RBSLs for Crude Oil Associated Wastes

Wastes from four different production areas plus oily soil or waste samples were analyzed for their equivalent carbon fractions. The analytical results were then used to calculate TPH RBSLs for each waste and the results are shown in Table 4. The non-residential RBSLs for the associated wastes are compared to those of the crude oils produced at the four sites.

Table 4. Non-residential RBSLs for crude oils and their associated wastes.

	Leaching to GW (mg/kg)	Outdoor Vaporization (mg/kg)	Non-Residential Surficial Soils (mg/kg)
Field #1			
Crude Oil	RES*	RES	67,000
Tank Bottoms	RES	RES	89,000
Oily Soil	RES	RES	80,000
Oiled Road Material	RES	RES	79,000
Field #2			
Crude Oil	RES	RES	46,000
Cyclone Separator Sludge	RES	RES	50,000
Slop Oil	RES	RES	53,000
Field #3			
Crude Oil	RES	RES	48,000
Oily Soil	RES	RES	59,000
Field #4			
Crude Oil	RES	RES	50,000
Oily Soil	RES	RES	58,000

Table 4 (Continued). Non-residential RBSLs for crude oils and their associated wastes.

	Leaching to GW (mg/kg)	Outdoor Vaporization (mg/kg)	Non-Residential Surficial Soils (mg/kg)
Field #5			
Tank Bottoms	RES	RES	56,000
Composted Tank Bottoms	RES	RES	52,000

*RES or residual saturation indicates that the oil does not pose a significant risk to human health even when present as residual material in soil.

For Field #1, the RBSLs for tank bottoms, soil from an old spill site (oily soil), and oiled road material are shown in comparison to the crude oil RBSL. This oil has an API gravity of 32.3° and is a waxy/paraffinic oil. The RBSLs for the wastes are higher than the crude oil RBSL. For Field #2, the RBSLs for cyclone separator sludge and slop oil are shown in comparison to that of the crude oil. This crude oil is a heavy oil, which has an API gravity of 19.4°. The RBSLs for wastes at both Field #1 and #2 are higher than that of the parent crude oils, largely due to the loss of volatile aromatic hydrocarbons from the wastes due to natural weathering processes. Weathering reduces the amounts of volatiles and increases the relative amount of waxes (high molecular weight aliphatics).

Oil impacted soil was collected at two different producing oilfields (Field #3,4) in the United States. These samples were analyzed, along with crude oil from each field, for their equivalent carbon number fractions. Table 4 lists the non-residential RBSLs for each of these samples. The oily soil samples yield consistently higher RBSLs compared to the parent crude oil from the field. As with the wastes from Fields #1 and #2, the higher RBSLs for the oily soils are due to the loss of volatile aromatic hydrocarbons from the soil. There is a definite trend for E&P wastes (tank bottoms, oiled road material, and oily soils) to have higher RBSLs than their parent crude oils. Therefore, the crude oil RBSLs presented in this chapter should be conservative for E&P wastes accidentally released or intentionally applied to soil (for example, landfarming).

RBSLs for Biodegraded Oily Wastes

The data from Field #5 (see Table 4) are for tank bottoms from a crude oil storage tank, and the same material after composting to reduce the hydrocarbon content via biodegradation. After composting, the RBSL was slightly lower, 52,000 mg/kg rather than 56,000 mg/kg TPH for the tank bottoms. This is because the more recalcitrant hydrocarbons (the large molecular weight aromatics) are present at higher concentrations as an overall percentage of the

oil, and this tends to drive the RBSL lower. The tank bottoms initially contained 498,000 mg/kg TPH and after composting the TPH level was reduced to 11,000 mg/kg, so the RBSL could be easily met via biodegradation processes/composting at this site.

RBSLs for Condensates

TPH RBSLs were developed for the 14 gas condensate samples. Figure 3 illustrates the results for non-residential surface soil exposure.

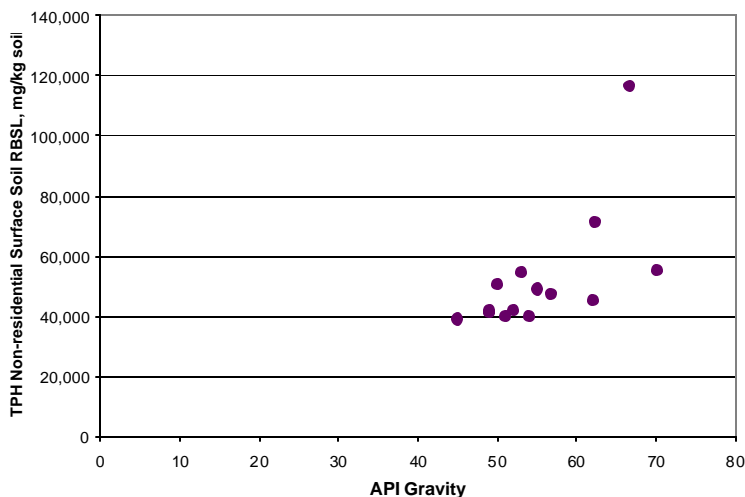


Figure 3. Non-residential surface soil TPH RBSLs calculated for 14 condensates plotted by their API gravity.

The TPH RBSLs are greater than or equal to 39,600 mg-TPH/kg-soil. Most of the condensates had non-residential surface soil RBSLs in the range of 40,000 to 60,000 mg/kg soil. The highest RBSL, 117,000 mg/kg soil, was obtained for a very light condensate that contained no aromatics $>C_{12}$. While there does not seem to be a good correlation between calculated RBSLs and API gravity, the data are plotted in this manner to illustrate the range of RBSLs obtained. Condensates can contain fairly high concentrations of benzene and since benzene is a carcinogen, it should be addressed separately at condensate spill sites as described in Chapter 11.

Recommendations on Use of RBSLs in the United States

The ranges of TPH RBSLs for crude oils and condensates at residential and non-residential sites are shown in Table 5. For both the residential and non-residential scenario, the only pathway posing a significant risk to human health is direct contact with contaminated soil (soil ingestion, inhalation of soil

particles, and dermal contact). The 95th percentile values for the crude oil RBSLs are also shown in Table 5. These 95th percentile values are recommended for establishing generic TPH Tier 1 RBSLs for all crude oil types, rather than the mean value or the minimum value. At individual E&P sites, use of generic TPH measurements should be sufficient to demonstrate whether or not Tier 1 levels have been attained. Since these 70 crude oils are representative of the composition of all crude oils produced around the world, there is no need to routinely analyze E&P site soils by the detailed fractionation analytical technique.

Table 5. Residential and non-residential RBSLs for crude oils and condensates (all data in mg/kg soil).

	Residential Summary Statistics (All Pathways)		Non-Residential Summary Statistics (All Pathways)	
	Crudes	Condensates	Crudes	Condensates
Mean	4,200	7,200	48,300	52,500
95%	2,800	5,000	41,300	39,600
Range				
Minimum	2,700	5,000	35,000	39,100
Maximum	6,300	18,000	67,300	117,000

Conclusions

TPH RBSLs have been calculated for crude oils based upon the specific composition of each oil. Since the crude oils analyzed to date reflect the composition of all crude oils produced around the world, there is no need to routinely analyze E&P site soils by a detailed fractionation analytical technique. Also, the RBSLs for E&P wastes were shown to be higher than the RBSL for fresh crude oil within a given production field. Therefore, the TPH RBSLs developed for crude oils are conservative for E&P associated wastes. The 95% RBSLs are recommended for use at crude oil and gas condensate spill sites. These RBSLs can be compared to TPH results obtained using simple, inexpensive analytical methods that have been used historically at E&P sites (these are described in Chapter 4 and include USEPA 418.1 and 8015).

There is no reason to perform the costly TPHCWG analytical fractionation method at most E&P sites, unless there is a need to do a site specific analysis. For example, site specific TPH fractionation data would be desirable if there is reason to believe that the Tier 1 RBSLs are too conservative, or if the spill occurs on residential property. This suggests that an E&P site can be adequately managed using generic TPH analyses (e.g., EPA Method 8015, Texas 1005, or other TPH measurements). These TPH results can then be compared to the Tier 1 RBSL values for crude oil and gas condensates presented in Table 5.

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Hydrocarbon Transport From Oil and Soil to Groundwater

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Introduction

The transport of hydrocarbons to groundwater is an important remediation consideration for many petroleum release sites. There is often a concern that hydrocarbons may leach from impacted soil, migrate to groundwater, and impact the water source at unacceptable levels. Simple screening level fate and transport models that do not account for Raoult's Law suggest that this potential exposure pathway may be of concern at many crude oil release sites. Incorporating Raoult's Law into the analysis indicates that crude oils generally have a limited potential to impact groundwater at levels that would present unacceptable human health risks.

Dissolved Hydrocarbons and Raoult's Law

As described in Chapter 6, the maximum dissolved concentration of a chemical in an organic mixture is a function of its pure compound solubility and the mole fraction of the chemical in the organic phase. When a chemical is part of an organic mixture, its solubility in water will be limited as follows:

$$C_{w\ max} = S_{eff} = x * S \quad (1)$$

where:

$C_{w\ max}$ = Maximum dissolved concentration of chemical in water (mg/L)

x = Mole fraction of chemical in organic chemical mixture (mole chemical/mole oil)

S = Solubility of pure chemical in water (mg/L)

S_{eff} = Effective solubility of chemical in water (mg/L)

Equation (1) is known as Raoult's Law and it is commonly used to predict the dissolved concentration of a chemical in water in contact with a hydrocarbon mixture. Raoult's Law is valid for compounds that are liquids at room temperature. For solid compounds, such as the larger polycyclic aromatic hydrocarbons (PAHs), the subcooled liquid solubility is used in place of the pure chemical solubility (S) in Equation (1).

When petroleum hydrocarbons (for example crude oil) are present as non-aqueous phase liquid (NAPL) in contact with groundwater, the dissolved concentrations of the individual chemicals are generally not affected by the amount of oil in contact with the water as illustrated below¹:

Mass of crude oil = mass of water:

Crude 1,000 mg/kg Benzene	Water 1.8 mg/L Benzene
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Mass of crude oil < mass of water:

Water 1.8 mg/L Benzene	
Crude: 1,000 mg/kg Benzene	

Mass of crude oil > mass of water:

Crude 1,000 mg/kg Benzene	
	Water: 1.8 mg/L Benzene

Since the effective solubility of any individual chemical depends on its concentration in the oil, but not on the amount of oil present [Equation (1)], compositional information for an oil can be used to determine if a given compound in oil, or the oil itself, could present a risk to groundwater. Raoult's Law can be used to predict the effective solubilities (i.e., the maximum dissolved concentrations) of compounds of interest. The predicted concentrations can then be compared to groundwater protection goals, and if the predicted values are less than the protection goals, then the oil cannot pose an unacceptable risk to human health via the groundwater ingestion pathway.

¹ Only when the mass of the crude oil is very low does the amount of the crude oil present affect the effective solubility of individual compounds. At low oil concentrations, lower final concentrations in both phases can be expected due to partitioning into the soil organic matter as illustrated in Figure 1.

Crude Oil Impacts on Groundwater

PAH and Benzene Impacts on Groundwater

In Table 1, Equation (1) and data from Chapters 10 and 11 were used to calculate maximum dissolved concentrations of aromatic compounds in water in contact with a crude oil. These values were then compared to United States groundwater protection regulations, in the form of United States Environmental Protection Agency (USEPA) Maximum Contaminant Levels (MCLs) for drinking water [1]. For chemicals that do not have MCLs, alternate health-based limits in the form of USEPA Region IX Preliminary Remediation Goals (PRGs) for tap water were used [2]. The PRGs are analogous to MCLs and are developed by USEPA using similar assumptions. Kerr et al. (2000) analyzed 60 oils for several aromatic compounds [3]. The highest concentration of each of four representative compounds ($C_{o \max}$ in the table) was used in this example and the molecular weight of the oil was assumed to be 200 g/mole. Since the highest concentration of each compound in any oil was used, this is a worst case evaluation.

Table 1. Calculated maximum dissolved concentrations, $C_{w \max}$, of selected aromatic compounds in crude oil.

	$C_{o \max}$ (mg/kg) ¹	X_{\max} ²	S^3 (mg/L)	$C_{w \max}$ (mg/L) ⁴	MCL ⁵ (mg/L)	PRG ⁶ (mg/L)	>MCL or PRG
Benzene	5,900	1.51E-02	1.80E+03	2.72E+01	5.0E-03	3.5E-04	Yes
Naphthalene	3,700	5.77E-03	1.03E+02	5.94E-01	NA	6.2E-03	Yes
Chrysene	120	1.05E-02	1.65E-01	1.74E-05	NA	9.2E-03	No
Benzo(a)pyrene	7.7	6.11E-06	4.00E-02	2.4E-07	2.0E-04	9.2E-06	No

- 1) $C_{o \max}$ = maximum concentration in crude oil (from measurements of 60 crude oils).
- 2) X_{\max} = maximum mole fraction (from measurements of 60 crude oils).
- 3) S = pure compound solubility. Values are from NMED Guidelines Table 4-3 [4]. Subcooled liquid solubility if solid at 25°C; calculated by multiplying the liquid solubility by the liquid-solid fugacity ratios from Peters et al. [5].
- 4) $C_{w \max}$ = maximum dissolved concentration, calculated from Equation (1).
- 5) Values for benzene and benzo(a)pyrene are USEPA MCLs (there are no USEPA MCLs for naphthalene and chrysene) [1].
- 6) USEPA Region IX Preliminary Remediation Goal (PRG) for tap water [2].

If any of the 60 crude oils were to be in direct contact with groundwater, benzene and naphthalene would be the only compounds that could possibly have dissolved concentrations that would exceed health-based limits. This same analysis was extended to 13 PAH compounds for which sufficient data were available. Even at the maximum concentrations for the 60 oils analyzed, the maximum dissolved concentrations for all PAHs, other than naphthalene, are below health-based limits as shown in Table 2.

Table 2. Calculated maximum dissolved concentrations of PAHs in crude oils.

PAH	Co max. (mg/kg) ¹	X max. ²	S (mg/L) ³	Cw max. (mg/L) ⁴	MCL ⁵ (mg/L)	PRG ⁶ (mg/L)	>MCL or PRG
Naphthalene	3,700	5.77E-03	1.03E+02	5.9E-01	NA	6.2E-03	Yes
Acenaphthene	58	7.52E-05	2.12E+01	1.6E-03	NA	3.7E-01	No
Anthracene	17	1.91E-05	4.43E+00	8.5E-05	NA	1.8E+00	No
Fluorene	380	4.57E-04	1.24E+01	5.7E-03	NA	2.4E-01	No
Benzo[a]anthracene	38	3.33E-05	2.35E-01	8.0E-06	NA	9.2E-05	No
Fluoranthene	26	2.57E-05	1.08E+00	2.8E-05	NA	1.5E+00	No
Chrysene	120	1.05E-04	1.65E-01	1.7E-05	NA	9.2E-03	No
Pyrene	82	8.1E-05	1.04E+00	8.4E-05	NA	1.8E-01	No
Dibenz[a,h]anthracene	9.2	6.60E-06	6.23E-01	4.0E-06	NA	9.2E-06	No
Benzo[a]pyrene	7.7	6.11E-06	4.00E-02	2.4E-07	2.0E-04	9.2E-06	No
Benzo[b]fluoranthene	14	1.11E-05	3.85E-02	4.2E-07	NA	9.2E-05	No
Benzo[k]fluoranthene	7	5.55E-06	6.15E-02	3.4E-07	NA	9.2E-04	No
Indeno[1,2,3-cd]pyrene	1.7	1.23E-06	5.50E-04	6.8E-10	NA	9.2E-05	No

- 1) $C_{o\ max}$ = maximum concentration in crude oil (from measurements of 60 crude oils).
- 2) X_{max} = maximum mole fraction (from measurements of 60 crude oils).
- 3) S = pure compound solubility. Values are from NMED Guidelines Table 4-3 [4]. Subcooled liquid solubility if solid at 25°C; calculated by multiplying the liquid solubility by the liquid-solid fugacity ratios from Peters et al. [5].
- 4) $C_w\ max$ = maximum dissolved concentration, calculated from Equation (1).
- 5) Value for benzo(a)pyrene is the USEPA MCL (there are no USEPA MCLs for the other PAHs) [1].
- 6) USEPA Region IX Preliminary Remediation Goal (PRG) for tap water [2].

TPH Impacts on Groundwater

TPH fractionation schemes are beginning to be used by state regulatory agencies within the United States to assess the potential migration and risks associated with petroleum hydrocarbons [6-10]. Raoult's Law can be used to evaluate the potential impacts of TPH on groundwater in the same way that it can be used to evaluate the potential impacts of benzene and PAHs. A similar exercise to that presented above for benzene and PAHs can be performed for TPH fractions. However, because there are no USEPA MCLs or PRGs for TPH or TPH fractions, the groundwater Protective Concentration Levels (PCLs) set by the Texas Natural Resource Conservation Commission (TNRCC) as groundwater protection goals are used for comparison [8]. In the TNRCC program, screening level (Tier 1) health-risk based PCLs are available for 12 TPH fractions for the ingestion of groundwater ($^{GW}GW_{Ing}$) exposure pathway.

By rearranging Equation (1), and substituting $^{GW}GW_{Ing}$ (multiplied by a dilution factor [8]) for $C_{w\ max}$, we can calculate the maximum concentration in the oil phase for each TPH fraction that would prevent TPH levels in groundwater from exceeding protective levels.

$$X = \frac{{}^{\text{GW}}\text{GW}_{\text{Ing}} * \text{LDF}}{S} \quad (2)$$

where:

${}^{\text{GW}}\text{GW}_{\text{Ing}}$ = PCL for ingestion of groundwater (mg/L). See Table 3 of [8].

LDF = Lateral dilution factor for groundwater (dimensionless) from Figure: 30 TAC §350.75 (b) of [8].

In Equation (2), the quantity ${}^{\text{GW}}\text{GW}_{\text{Ing}} * \text{LDF}$ is equal to the effective solubility [$C_{w \text{ max}}$ in Equation (1)] and represents the water concentration in direct contact with soil and residual oil. The terms ${}^{\text{GW}}\text{GW}_{\text{Ing}}$ and LDF are used here to be consistent with notation used in the TNRCC rules.

Table 3 presents groundwater protection levels for various aromatic and aliphatic fractions, their respective pure solubilities, and the calculated maximum acceptable oil mole fractions for these fractions. These data indicate that the levels for the various aromatic fractions in crude oil can be greater than 9 mole %. Note that for all aliphatic fractions with carbon numbers greater than 6 and for aromatic fractions with carbon numbers greater than 12, even if these fractions existed as a pure liquid in soil, they could not pose an unacceptable risk to human health based on the groundwater ingestion pathway.

Table 3. Calculated mole fractions in oil for various TPH fractions.

	${}^{\text{GW}}\text{GW}_{\text{Ing}}^1$ (mg/L)	S^2 (mg/L)	χ Concentration in TPH (Mole Fraction)
>C ₇ -C ₈ Aromatics (TPH)	2.4	530	0.09
>C ₈ -C ₁₀ Aromatics (TPH)	0.98	65	0.30
>C ₁₀ -C ₁₂ Aromatics (TPH)	0.98	25	0.78
>C ₁₂ -C ₁₆ Aromatics (TPH)	0.98	5.8	1
>C ₁₆ -C ₂₁ Aromatics (TPH)	0.73	0.65	1
>C ₂₁ -C ₄₄ Aromatics (TPH) ³	0.73	0.0066	1
C ₆ Aliphatics (TPH)	1.5	36	0.83
>C ₆ -C ₈ Aliphatics (TPH)	1.5	5.4	1
>C ₈ -C ₁₀ Aliphatics (TPH)	2.4	0.43	1
>C ₁₀ -C ₁₂ Aliphatics (TPH)	2.4	0.034	1
>C ₁₂ -C ₁₆ Aliphatics (TPH)	2.4	0.00076	1
>C ₁₆ -C ₄₄ Aliphatics (TPH) ³	49	2.5E-06	1

- 1) From Table 3 of Texas Risk Reduction Program Rules (TRRP). Corresponding to a residential land use scenario. LDF = 20.
- 2) From Figure: 30 TAC §350.73 (e) of TRRP Rules.
- 3) Extended for the C₃₅ to C₄₄ equivalent carbon number range for crude oils. Values listed are from TRRP Rules for up to C₃₅.

Another interpretation of the data in Table 3 is that if the concentrations of these fractions in a crude oil (or petroleum hydrocarbon mixtures in general) are below those shown in Table 3, then no amount of TPH in the soil could produce groundwater concentrations that would exceed protective levels. In this case, acceptable TPH levels in soil would be limited by other exposure pathways, rather than by leaching to groundwater. In general, this technique could be used as a screening method for evaluating the potential of any given oil to produce groundwater TPH levels that would exceed groundwater protective levels.

Impact of Soil Organic Content on Partitioning

When two organic phases and water are in contact, a chemical will partition between the three phases. The equilibrium concentration in each phase will depend on the relative affinity of the chemical for the three phases. In the following example, the affinity of the chemical is 100 times greater for Phase 1 than water, and 75 times greater for Phase 2 than water. This is similar to the relative affinity of petroleum hydrocarbons for oil and soil organic matter, respectively. At equilibrium, the ratio of the concentration of a chemical in the three phases remains constant at 100:75:1.

Organic Phase 1 100 mg/kg	Water 1 mg/L
Organic Phase 2 75 mg/kg	

In unimpacted soil, both the soil organic content (SOC) and water are free of petroleum hydrocarbons. When oil is added to soil, an individual chemical contained in the oil will partition between the oil, SOC, and water. At low oil levels, the concentration of the chemical in the oil phase decreases due to loss to the SOC and water. This results in a lower dissolved concentration than would be expected for oil-water partitioning alone. As the mass of oil increases relative to the SOC, the final organic phase concentration remains closer to the initial oil concentration. The dissolved concentration gets closer to, but cannot exceed, the effective solubility predicted by Raoult's Law.

The partitioning between oil, SOC, and water is demonstrated in the following example. The concentration of the chemical of interest is initially 1,000 mg/kg in the oil phase. Raoult's Law predicts a maximum dissolved concentration of 10 mg/L. The amount of oil ranges from 100 to 10,000 mg/kg soil. The SOC is 1,000 mg/kg soil. C_{of} is the final concentration of the compound in the oil phase. C_s is the concentration in the SOC phase and C_w is the dissolved phase.

The dissolved concentration never exceeds the 10 mg/L effective solubility predicted by Raoult's Law.

Table 4. Partitioning behavior of a chemical between oil, SOC, and water.

Amount of Oil (mg/kg)	Amount of SOC (mg/kg)	Final Conc. in Oil Phase (C_o – mg/kg)	Conc. of Chemical in SOC Phase (C_s – mg/kg)	Conc. of Chemical in Dissolved Phase (C_w – mg/L)
100	1,000	118	88	1.18
1,000	1,000	571	429	5.71
10,000	1,000	930	698	9.30

Figure 1 shows the same effect over a wider range of concentrations. The dissolved concentration of the compound increases with oil concentrations at low levels, but the maximum dissolved concentration remains limited to the value predicted by Raoult's Law.

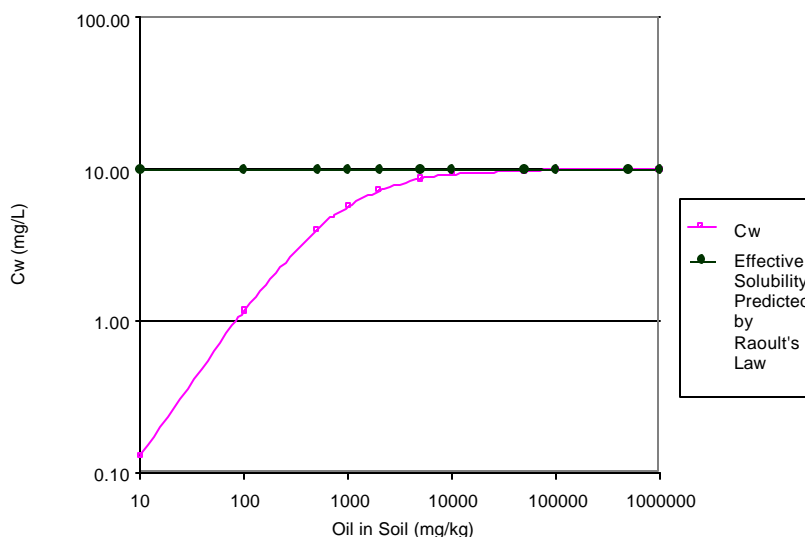


Figure 1. The partitioning behavior of a chemical between dissolved and soil phases.

The partitioning of organic compounds between the SOC and water is the basis for setting soil screening levels that are protective of groundwater. The USEPA Soil Screening Guidance presents the following equation for relating soil concentrations to dissolved concentrations [11]:

$$C_s = C_w * [K_d + ((T_w + T_a K_H)/?_b))] \quad (3)$$

where:

C_s = Soil screening level (mg/kg)

C_w = Dissolved groundwater protection goal (mg/L)

K_d = Soil-water sorption coefficient (mg/kg dry soil)/(mg/L water)

T_w = Water filled porosity (cm³ water/cm³ soil)

T_a = Air filled porosity (cm³ air/cm³ soil)

K_H = Henry's Law coefficient (mg/L vapor/mg/L water)

$?_b$ = Soil bulk density (g dry soil/cm³ soil)

The component of the equation ' $(T_w + T_a K_H)/?_b$ ' takes into account the fraction of the COCs in the water and vapor phase. Since this term is typically much smaller than K_d , Equation (3) can be simplified for this discussion to:

$$C_s = C_w * K_d \quad (4)$$

The soil / water sorption coefficient K_d is a function of the amount of organic phase associated with the soil, and the K for that organic phase. For a soil in the absence of a NAPL or oil phase [12]:

$$K_d = K_{oc} * foc \quad (5)$$

where:

K_{oc} = SOC / water partition coefficient (mg /kg SOC)/(mg /L water)

foc = The fraction of organic carbon in the soil (kg SOC/kg soil)

If two organic phases are present, the organic carbon in the soil and the oil, then the soil-water sorption coefficient in Equation (4) can be redefined as:

$$K_d = (K_{oc}^1 * f_{oc}^1) + (K_{oc}^2 * f_{oc}^2) \quad (6)$$

An oil impacted soil has two organic phases, the SOC and the oil. By replacing K_{oc}^2 with K_{oil} (mg/kg oil)/(mg/L water), and f_{oc}^2 with the oil concentration in the soil (kg oil/kg soil), K_d from Equation (6) can be inserted into Equation (4):

$$C_s = C_w * ((K_{oc} * f_{oc}) + (K_{oil} * f_{oil})) \quad (7)$$

K_{oil} can be calculated using Raoult's Law:

$$K_{oil} = \frac{MW_i}{S_i \cdot MW_o} (10^6 \text{ mg / kg}) \quad (8)$$

where:

MW_i = Molecular weight of the compound (g/mole)

MW_o = Average molecular weight of the TPH (g/mole)

S_i = Solubility of the compound of interest (mg/L)

Summary

The protection of groundwater is a critical component of environmental management at sites impacted with petroleum hydrocarbons. The potential for chemicals of concern to leach from oil or petroleum impacted soil must be understood in order to accurately assess the risk to human health from the ingestion of groundwater. In this chapter, the technical basis for calculating maximum dissolved hydrocarbon concentrations in leachate was presented. If the concentration of a constituent in either the oil or soil phase is known, the maximum dissolved concentration can be calculated. The dissolved concentration is limited by equilibrium partitioning between the oil and water phases. Partitioning between soil organic matter and these phases can further reduce the dissolved hydrocarbon leachate concentration. The analysis of crude oil data presented in this chapter illustrates that benzene and naphthalene may potentially leach from crude oil-containing soil to groundwater at levels that may pose an unacceptable risk to human health. The other priority pollutant PAHs are not present in crude oil at high enough concentrations to be a potential threat to groundwater via leaching from soil.

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Risk-Based Soil Screening Levels for Crude Oil: The Role of Polyaromatic Hydrocarbons

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Introduction

Polyaromatic hydrocarbons (PAHs) are ubiquitous in the environment and result from both naturally-occurring and man-made sources. PAHs can be formed whenever organic substances are exposed to high temperatures. Some PAHs are also synthesized by several species of plants and bacteria [1]. The largest single source of PAHs to the environment is likely the residential burning of wood [2]. Combustion of fossil fuels is also a major source, with other sources including volcanoes, agricultural burning, asphalt roads, and forest fires [2]. In the home, PAHs can be found in tobacco smoke, grilled and smoked foods, wood-burning fireplaces, meat, processed or pickled foods, and beverages.

Most of the direct releases of PAHs are to the atmosphere, and most of these are associated with particulate matter. Settling of the particulates allows PAHs to be redistributed to other environmental media, such as soil and water. PAHs are found in relatively high concentrations at certain types of industrial sites, particularly in contaminated soils at manufactured gas plants (MGP) and wood-treatment facilities. Creosote, a common wood preservative, is a distillate of coal tar (distilled from coal at high temperatures in the absence of oxygen), and contains higher concentrations of PAHs than many other substances [3].

At sufficient dose levels, laboratory studies show that some PAHs cause adverse health effects including cancer and reproductive difficulties in animals. People exposed for long periods of time to mixtures of chemicals that include PAHs can also develop cancer [2]. Therefore, PAHs have been identified as chemicals of potential environmental concern, and PAHs known to cause adverse effects have been placed on the United States Environmental Protection Agency (USEPA) priority pollutant list.

The structures of the 16 PAHs currently on the USEPA priority pollutant list are shown in Figure 1. Selected physical-chemical properties for these PAHs are given in Table 1. Boiling points range from 217 to 542°C and aqueous solubilities of pure solids range from 0.00026 to 31 mg/L.

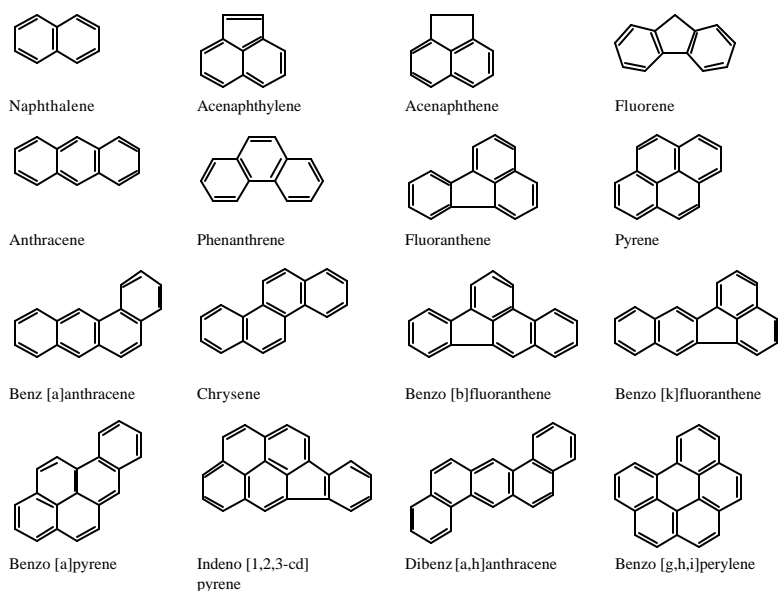


Figure 1. Chemical structures of the 16 USEPA priority pollutant PAHs.

Table 1. Names and selected physical-chemical properties of the 16 USEPA priority pollutant PAHs [4,5,6].

PAH	Boiling Point ¹ (°C)	Aqueous Solubility of Pure Solid (mg/L)	Aqueous Solubility of Pure Subcooled Liquid (mg/L)	log K _p ¹	Vapor Pressure (Torr at 20°C)
Naphthalene	217	31	103.23	3.37	4.92 x 10 ⁻²
Acenaphthene	279	3.8	19	4.33	2.0 x 10 ⁻²
Acenaphthylene	265	16.1	73.094	4.07	2.9 x 10 ⁻²
Anthracene	340	0.045	4.59	4.45	1.96 x 10 ⁻⁴
Phenanthrene	340	1.1	4.07	4.46	6.80 x 10 ⁻⁴
Fluorene	293	1.9	11.875	4.18	1.3 x 10 ⁻²
Fluoranthene	295	0.26	5.26	5.33	6.0 x 10 ⁻⁶
Benz[a]anthracene	400	0.011	0.275	5.61	5.0 x 10 ⁻⁹
Chrysene	448	0.0015	0.1545	5.61	6.3 x 10 ⁻⁷
Pyrene	360	0.132	1.015	5.32	6.85 x 10 ⁻⁷
Benzo[a]pyrene	496	0.0038	0.1265	6.04	5.0 x 10 ⁻⁷
Benzo[b]fluoranthene	481	0.0015	0.0384	6.57	5.0 x 10 ⁻⁷
Benzo[k]fluoranthene	480	0.0008	0.0615	6.84	5.0 x 10 ⁻⁷
Dibenzo[a,h]anthracene	535	0.0005	0.125	5.97	1.0 x 10 ⁻¹⁰
Benzo[g,h,i]perylene	542	0.00026	0.0866	7.23	1.0 x 10 ⁻¹⁰
Indeno[1,2,3-cd]-pyrene	530	0.062	1.55	7.66	1.0 x 10 ⁻¹⁰

1) LogK_p = Logarithm of the soil:water partition coefficient.

PAHs occur naturally in crude oils. While crude oils and their associated wastes contain PAHs, there are few published data on the amounts of priority pollutant

PAHs in exploration and production (E&P) wastes. The American Petroleum Institute (API) analyzed crude oil-containing soils and tank bottoms for chrysene, naphthalene, phenanthrene, and 1-methyl naphthalene [7]. In 1994, the USEPA Office of Solid Waste sampled crude oil tank bottom wastes and analyzed them for semi-volatile organics including naphthalene, phenanthrene, fluorene, and chrysene [8]. Neither of these studies examined the entire suite of priority pollutant PAHs in E&P wastes. However, their results indicate that the distribution pattern and concentrations of PAHs in crude oils probably differ in many respects from those found in soils containing PAHs from MGP and wood-treating facilities.

Except for the State of California, state regulatory agencies in the United States do not require routine analysis of PAHs in wastes or soils at E&P sites. However, at some E&P sites, PAHs have been included in site characterization and risk assessment activities. It is important to understand the types and concentrations of priority pollutant PAHs in crude oils and their associated wastes in risk-based decision-making (RBDM) for E&P sites.

Analytical Methodology

Sixty crude oils from production sites around the world were analyzed for the 16 priority pollutant PAHs. Figure 2 illustrates the sources of the crude oils, by geographic region. The crude oils were selected based on their diversity in API gravities and compound classes. The goal was to analyze a diverse group of oils that would represent the range of crude oil types produced around the world. In addition to the 60 crude oils, 10 condensates, 10 oily wastes (tank bottoms, sludges, etc.), and 6 oil-containing soils also were analyzed for their PAH content.

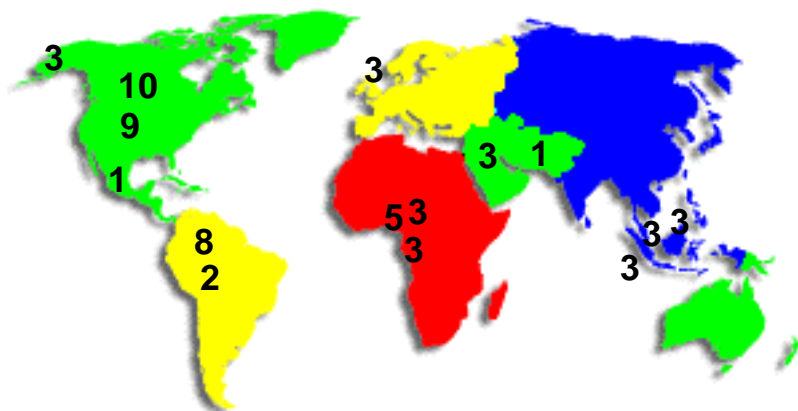


Figure 2. Number of crude oil samples (60 total) analyzed by the geographic region from which they originated.

Using pentane, a dilution was prepared for each crude oil and condensate to obtain an approximate concentration of 5 mg/mL. Each dilution was then spiked directly with the following surrogates; naphthalene-_{d8}, acenaphthene-_{d10}, phenanthrene-_{d10}, and benzo[a]pyrene-_{d12}. Extracts were obtained from wastes and soils using either methylene chloride or pentane as the solvent. The diluted crude oils and extracts were then passed through a silica gel chromatography column to separate the aromatic hydrocarbons using modified USEPA Method 3630. Pentane was used to elute the saturate fraction, methylene chloride:pentane (50:50) was used to elute the aromatic hydrocarbons. The aromatic fraction was concentrated and spiked with the following internal standards; chrysene-_{d12} and fluorene_{d10}.

To determine the concentrations of selected PAHs, the concentrated extracts and diluted crude oils were analyzed by gas chromatography/mass spectrometry (GC/MS) operated in the selected ion monitoring (SIM) mode using a modified USEPA Method 8270. A five-point calibration, an Instrumental Reference Material (NIST IRM 1491), and an oil reference standard (Alaska North Slope crude oil) were analyzed at the beginning of each instrumental sequence. All instruments were calibrated with analytical standards prior to the analysis of the samples. Target analyte concentrations of the 16 priority pollutant PAHs were calculated versus the internal standard compound and were corrected for recovery efficiency of the surrogate compounds. The recovery of the surrogate compounds was calculated relative to the internal standards added to the samples prior to instrumental analysis.

PAH Content of Analyzed Samples

The range and mean concentration of each of the priority pollutant PAHs as well as the detection frequency for crude oils and condensates are provided in Tables 2a and 2b. Naphthalene, phenanthrene, fluorene, chrysene, pyrene, and benzo[b]fluoranthene occurred in >97% of the crude oils tested. Anthracene, fluoranthene, dibenz[a,h]anthracene, and indeno[1,2,3-cd]pyrene were less frequently detected (40% of oils contained anthracene and fluoranthene, and <7% contained indeno[1,2,3-cd]pyrene). Acenaphthylene was not detected in any of the 60 crude oils.

Table 2a. PAH content of 60 crude oils (all data are reported in mg/kg oil).

PAH	Minimum (mg/kg)	Maximum (mg/kg)	Mean (mg/kg)	Detection Frequency (%)
Naphthalene	1.2	3700	422.9	100
Acenaphthylene	ND	NA	NA	0
Acenaphthene	ND	58	13.9	80
Anthracene	ND	17	3.4	40
Phenanthrene	ND	916	176.7	98
Fluorene	1.4	380	73.6	100
<i>Benz[a]anthracene</i>	ND	38	5.5	67
Fluoranthene	ND	26	3.9	40
<i>Chrysene</i>	4	120	28.5	100
Pyrene	ND	82	15.5	97
<i>Dibenz[a,h]anthracene</i>	ND	9.2	1.0	47
<i>Benzo[a]pyrene</i>	ND	7.7	2.0	75
<i>Benzo[b]fluoranthene</i>	ND	14	3.9	100
<i>Benzo[k]fluoranthene</i>	ND	7	0.46	93
<i>Indeno[1,2,3-cd]pyrene</i>	ND	1.7	0.06	7
Benzo[g,h,i]perylene	ND	9.6	1.53	63

Table 2b. PAH content of 10 condensates (all data are reported in mg/kg condensate).

PAH	Minimum (mg/kg)	Maximum (mg/kg)	Mean (mg/kg)	Detection Frequency (%)
Naphthalene	200	5,700	1,690	100
Acenaphthylene	ND	9.2	1.15	10
Acenaphthene	ND	12	1.43	10
Anthracene	ND	27	5.91	50
Phenanthrene	ND	250	90	90
Fluorene	3.9	82	44.8	100
<i>Benz[a]anthracene</i>	ND	0.78	0.30	10
Fluoranthene	ND	11	2.47	30
<i>Chrysene</i>	ND	5.5	1.93	40
Pyrene	ND	12	2.96	40
<i>Dibenz[a,h]anthracene</i>	ND	NA	NA	0
<i>Benzo[a]pyrene</i>	ND	NA	NA	0
<i>Benzo[b]fluoranthene</i>	ND	2	0.64	30
<i>Benzo[k]fluoranthene</i>	ND	NA	NA	0
<i>Indeno[1,2,3-cd]pyrene</i>	ND	NA	NA	0
Benzo[g,h,i]perylene	ND	NA	NA	0

PAHs in ***bold italic*** have been shown to be carcinogenic in laboratory animals [9].

ND = Below detection limits. Detection limit = 0.50 mg/kg.

Mean determined using one-half the detection limit for non-detect samples.

NA = Not applicable since no PAH was detected.

A significant health concern resulting from exposure to PAHs is their potential for carcinogenicity, which is chemical-structure dependent. Three-ring PAHs, including anthracene and fluorene, have not been shown to cause cancer in laboratory animals [2]. On the other hand, there are seven 4 to 6-ring PAHs (shown in bold type in Tables 2a and 2b) that are carcinogenic in laboratory animals [2]. Of the PAHs shown to be carcinogenic, chrysene was found at the highest concentrations in crude oil (its mean concentration was 28.5 mg/kg oil). The mean concentrations in crude oil of the other carcinogenic PAHs range from 5.5 mg/kg oil for benz[a]anthracene, to <0.5 mg/kg oil for benzo[k]fluoranthene and indeno[1,2,3-cd]pyrene. The mean concentration of benzo[a]pyrene was 2.0 mg/kg oil.

The range and mean concentrations of PAHs detected in ten condensate samples is presented in Table 2b. Overall, PAHs were detected in condensates much less frequently than in crude oils. Naphthalene, fluorene, and phenanthrene were detected in >90% of the samples, while dibenz[a,h]anthracene, benzo[a]pyrene,

benzo[k]fluoranthene, indeno[1,2,3-cd]pyrene, and benzo[g,h,i]perylene were not detected in any sample. Only three of the seven carcinogenic PAHs (benz[a]anthracene, chrysene, and benzo[b]fluoranthene) were detected in the condensates. Naphthalene represents >90% of the total priority pollutant PAHs present in condensates.

Table 3 compares the PAH content of soils from contaminated creosote production and MGP sites [10,11] with the concentrations of PAHs found in the ten E&P wastes (sludges/tank bottoms) and six crude oil-containing soils that were analyzed as part of this study. The concentration of PAHs in E&P wastes clearly was markedly lower than in site soils affected by creosote or MGP operations. Furthermore, the distribution of the individual PAHs differ markedly, with E&P wastes containing very small amounts of 4-, 5-, and 6-ring PAHs, compared to MGP site soils.

Table 3. Mean PAH concentrations present in creosote, MGP, sludges/tank bottoms, and E&P soils.

PAH	Soil Concentrations Creosote Production Sites Mean ^[10] (mg/kg)	Soil Concentrations MGP Sites Mean ^[11] (mg/kg)	Sludges/ Tank Bottoms Mean (mg/kg)	Soil Concentrations E&P Sites Mean (mg/kg)
Naphthalene	1,313	---	44.00	0.183
Acenaphthylene	33	2	0.29	0.017
Acenaphthene	---	---	6.51	0.733
Fluorene	650	225	21.09	0.455
Anthracene	334	156	2.22	0.214
Phenanthrene	1,595	379	55.53	1.429
Fluoranthene	682	2,174	2.31	0.283
Pyrene	642	491	5.42	0.869
Benzo[a]anthracene	---	317	2.98	0.393
Chrysene	614	345	12.16	1.385
Benzo[b]fluoranthene	---	260	1.74	0.199
Benzo[k]fluoranthene	---	238	0.28	0.061
Benzo[a]pyrene	---	92	0.97	0.119
Indeno[1,2,3-cd]pyrene	---	207	0.20	0.024
Dibenz[a,h]anthracene	---	2,451	0.65	0.094
Benzo[g,h,i]perylene	---	---	0.73	0.176

These differences in PAH concentration and distribution are also illustrated in Figure 3, which compares the mean value for each of the carcinogenic PAHs in E&P pit sludges/tank bottoms, soils, condensates, and crude oils with those in coal tar. Coal tar contains approximately 1,000 times more carcinogenic PAHs than do crude oils, and 10,000 times more than condensates. The most abundant

carcinogenic PAHs in crude oils are benz[a]anthracene and chrysene; while in condensates, chrysene and benzo[b]fluoranthene are the most abundant.

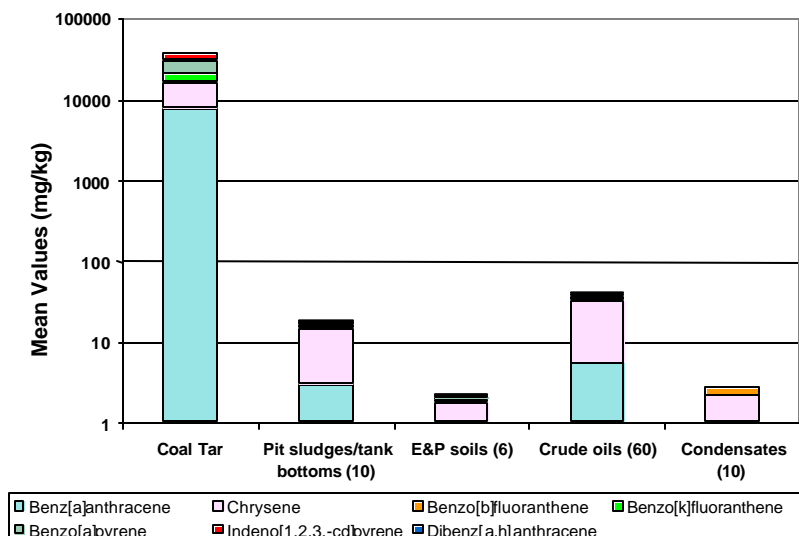


Figure 3. Distribution fingerprints of the carcinogenic PAHs found in 60 crude oils, 10 condensates, 6 oily soils, and 10 pit sludges/tank bottoms from E&P sites in comparison to those in coal tar [12].

Some differences in the concentrations of 4-6 ring PAHs were noted when comparing crude oils produced from different regions of the world. For example, the PAH content is greater, on average, in crude oils produced in Indonesia and Africa, compared to the oils produced in North America. Further analysis of this phenomenon revealed that those oils with higher concentrations of 4-6 ring PAHs are from lacustrine (lakebed) source rocks in Indonesia and Africa. Lacustrine source crude oils are rare in North America. In addition, the highest concentrations of 4-6 ring PAHs were present in those lacustrine source oils that had been biodegraded in the oil reservoir, as shown in Figure 4.

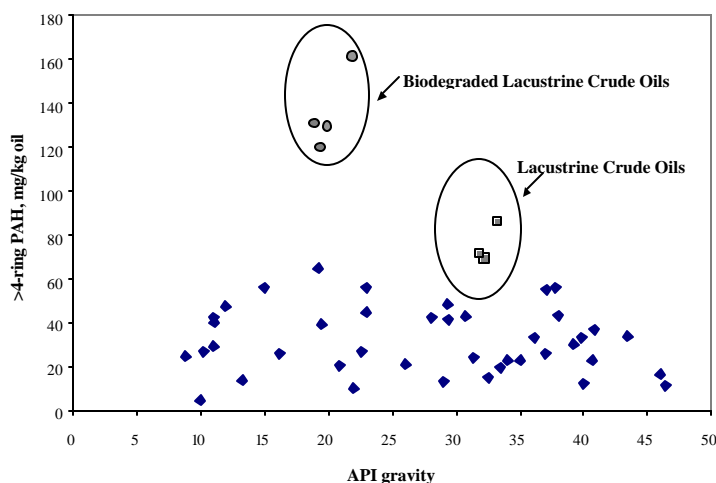


Figure 4. Concentration of 4-6 ring PAHs versus API gravity of crude oils. Crude oils from lacustrine sources that have been biodegraded contain the highest concentrations of >4-ring PAHs.

Figure 4 also illustrates that API gravity is not a good predictor of the concentration of 4 to 6-ring PAHs that may be present in crude oils. Source rock and maturity have been reported to correlate with PAH content of crude oils [13].

Risk-Based Screening Levels for PAHs

Chemical-specific Risk-Based Screening Levels (RBSLs) can be derived for the individual 16 priority pollutant PAHs. Regulatory agencies in several of the major oil producing states in the United States have developed RBSLs or protective concentration levels (PCLs) for PAHs. The approaches and algorithms used by the agencies to derive Tier 1 levels generally follow those used by the USEPA in deriving Preliminary Remediation Goals (PRGs) [14] and Soil Screening guidance levels (SSLs) [15], or those described by the American Society for Testing and Materials (ASTM) “Standard Guide for Risk-Based Corrective Action Applied at Petroleum Release Sites” [16].

Table 4 summarizes the Tier 1 RBSLs developed by state agencies in major oil producing states for the 16 priority pollutant PAHs. The variability in Tier 1 levels between states is due, in part, to policy decisions regarding acceptable target risk levels. Different regulatory agencies have adopted different target risk levels, so that some Tier 1 levels represent those concentrations that would result in a cancer risk of one-in-a-hundred thousand (1×10^{-5}), while others represent a one-in-a-million (1×10^{-6}) target risk. For example, the State

Table 4. Tier 1 RBSLs from major oil producing states showing the concentration of each PAH for soils in residential or industrial areas, plus those concentrations of crude oil in soil that are protective of groundwater. All units are in mg/kg.

PAH	Alaska ¹	Louisiana ²			New Mexico ³			Texas ⁴		
		Industrial	Residential	GW Protect	Industrial	Residential	GW Protect	Industrial	Residential	GW Protect
Naphthalene	38-43	44	6.3	1.5	18,500	1,790	0.68	360	220	31
Acenaphthylene	NA	NA	NA	NA	NA	NA	NA	37,000	3,800	410
Acenaphthene	190-210	3,900	260	220	27,700	2,900	187.95	37,000	3,000	240
Fluorene	240-270	3,100	180	230	19,600	2,150	196.12	25,000	2,300	300
Anthracene	3,900-4,300	25,000	1,400	120	157,000	16,900	4,499.81	190,000	18,000	6,900
Phenanthrene	NA	NA	NA	NA	14,500	1,590	270.07	19,000	1,700	420
Fluoranthene	NA	3,600	200	1,200	22,100	2,340	1,247.59	25,000	2,300	1,900
Pyrene	1,400-1,500	2,700	150	1,100	16,700	1,760	1,301.71	19,000	1,700	1,100
Benz[a]anthracene	5.5-6	3.6	0.56	8.6	21.8	9.49	7.48	24	5.7	18
Chrysene	550-620	400	61	76	2,150	940	810.27	2,400	560	1,500
Benzo[b]fluoranthene	17-20	3.6	0.56	29	21.7	9.45	25.68	24	5.7	60
Benzo[k]fluoranthene	170-200	35	5.5	120	21.9	9.52	25.68	240	57	620
Benzo[a]pyrene	2.4-3	0.36	0.33	23	2.19	0.952	4.74	2.4	0.56	7.6
Indeno[1,2,3-cd]pyrene	50-54	3.6	0.56	9.2	NA	NA	NA	24	5.7	170
Dibenz[a,h]anthracene	5-6	0.36	0.33	540	2.21	0.952	3.74	2.4	0.55	15
Benzo[g,h,i]perylene	NA	NA	NA	NA	NA	NA	NA	19,000	1,800	46,000

NA = Not available.

- 1) Cleanup levels based on migration to groundwater assuming over 40-inch and under 40-inch rainfall zones, respectively. Cleanup levels correspond with Alaska AK101-103AA and AK101-103 methods. Source: ADEC, 2000 [18].
- 2) Soil screening standards for industrial exposures, non-industrial exposures, and protection of groundwater. Source: LDEQ RECAP, 2000 [19].
- 3) Industrial and residential direct contact exposures, and Tier 1 levels protective of groundwater assuming a DAF = 1. Source: NMED, 2000 [20].
- 4) Industrial and residential direct contact exposures and protection of groundwater assuming a 0.5-acre source. Source: TNRCC, 2001 [21].

of Louisiana uses a target risk of 1×10^{-6} for carcinogens and a Hazard Quotient (HQ) of 0.1 for non-carcinogens, while Texas uses 1×10^{-5} for carcinogens and a HQ = 1.0. In any case, both of these target cancer risk values lie within the acceptable target risk range of 1×10^{-6} to 1×10^{-4} set by USEPA for evaluating contaminated sites under Superfund [17] and are in line with target risk levels commonly adopted by regulatory agencies for environmental programs in many states.

Acceptable Total Petroleum Hydrocarbon (TPH) Levels That Are Protective for PAHs

The maximum concentrations of each of the PAHs detected in crude oils and condensates listed in Tables 2a and 2b were compared to the lowest state Tier 1 residential RBSL listed in Table 4. This comparison was done to determine the acceptable oil concentration in soil [in terms of its TPH content] that would result in no PAH being above any single residential or groundwater protection Tier 1 level. In reality, for all non-carcinogenic PAHs (except benzo[g,h,i]perylene), the lowest Tier 1 RBSL is for groundwater protection. Tier 1 RBSLs that are protective of direct residential exposure to impacted soils are higher (i.e., less stringent) than groundwater protection levels. The lowest Tier 1 RBSLs for carcinogenic PAHs and benzo[g,h,i]perylene are based on direct residential exposure to impacted soils.

The following formula was used to estimate acceptable TPH levels in soil that would assure that all PAH levels were below their respective individual RBSLs:

$$\text{Acceptable TPH (\% Oil in Soil)} = \text{RBSL (mg PAH/kg Soil)} / \text{C}_{\text{oil}} \text{ (mg PAH/kg Oil)} * 100$$

The acceptable TPH level was estimated for each oil or condensate, and the results are shown in Table 5. For the crude oils, the estimated acceptable TPH levels ranged from 1.4 to >100%, except for the case of naphthalene. For the condensates, the estimated acceptable TPH levels in soil range from 28 to >100%. Again, naphthalene is an exception, resulting in an acceptable concentration of condensate in soil as low as 0.012%. This TPH level is protective of groundwater resources. Acceptable TPH levels for direct residential contact with impacted soils would be higher.

Naphthalene may be present in some crude oils and condensates at concentrations that exceed Tier 1 PAH levels even at low TPH levels. Naphthalene may be of particular concern for protecting groundwater resources. However, the acceptable oil and condensate concentrations provided in Table 5 are for fresh spills. Natural attenuation of naphthalene due to weathering (volatilization and biodegradation) may occur quickly at some spill sites. Also, Tier 1 RBSLs for naphthalene do not consider the impact of Raoult's Law as described in Chapter 9. For these reasons, the preferred method for assessing

risk due to naphthalene is to analyze specifically for naphthalene in soil, rather than setting very low Tier 1 levels for TPH. This is consistent with the approach for benzene described in Chapter 11.

Fifteen of the priority pollutant PAHs should not be present above any residential Tier 1 level at either fresh crude oil or condensate spill sites, as long as TPH levels are less than 1.0% (10,000 mg/kg). Therefore, there is no need to routinely use USEPA Method 8270 to quantify these 15 PAHs at E&P spill sites. The only PAH that may be present at concentrations of concern is naphthalene, and it can be analyzed using USEPA Method 8260 for volatiles. Eliminating the use of USEPA Method 8270 for all priority pollutant PAHs at E&P spill sites is cost-effective, while still being protective of human health.

Table 5. Comparison of lowest Tier 1 levels in major oil producing states with the maximum concentration of PAH observed in crude oils and condensates.

PAH	Lowest Tier 1 RBSL From Table 4 (mg/kg Soil)	Maximum Observed Concentration (mg/kg Oil)		Acceptable Concentration for a Fresh Spill (% Oil or Condensate in Soil)	
		Crude Oils	Condensates	Crude Oil in Soil	Condensate in Soil
Naphthalene	0.68	3,700	5,700	0.018	0.012
Acenaphthylene	410	ND	9.2	>100	>100
Acenaphthene	187.95	58	12	>100	>100
Fluorene	180	380	82	47.3	>100
Anthracene	120	17	27	>100	>100
Phenanthrene	270.07	916	250	29.5	>100
Fluoranthene	200	26	11	>100	>100
Pyrene	150	82	12	>100	>100
<i>Benz[a]anthracene</i>	0.56	38	0.78	1.4	71.8
<i>Chrysene</i>	61	120	5.5	50.8	>100
<i>Benzo[b]fluoranthene</i>	0.56	14	2	4.0	28.0
<i>Benzo[k]fluoranthene</i>	5.5	7	ND	78.5	>100
<i>Benzo[a]pyrene</i>	0.33	7.7	ND	4.2	>100
<i>Indeno[1,2,3-cd]pyrene</i>	0.56	1.7	ND	32.9	>100
<i>Dibenzo[a,h]anthracene</i>	0.33	9.2	ND	3.5	>100
<i>Benzo[g,h,i]perylene</i>	1800	9.6	ND	>100	>100

ND = Below detection limits.

This examination of PAH content of oils and condensates applies to situations involving a single oil spill incident or single application of oil. Sites that have received multiple applications of crude oil or oil-contaminated soils, e.g., a land farm site or an old pit, would require additional consideration.

Summary

Sixty crude oils and ten condensates were analyzed for their concentrations of 16 priority pollutant PAHs. Screening of the human health risk associated with

soil containing crude oil or condensate showed the risk for 15 of the 16 PAHs was not significant at TPH concentrations well above 10,000 ppm, the current TPH soil management level in many states. Naphthalene is the only PAH that may be present in crude oils or condensates at concentrations that may pose a risk at oil concentrations of 1% or lower. The limiting exposure pathway for naphthalene is leaching from soil to groundwater and protection of groundwater resources, rather than direct residential exposure to contaminated surface soils.

Overall, this work indicates that the low levels of PAHs in crude oils are unlikely to be a major risk management consideration at crude oil or condensate spill sites. This constitutes compelling evidence that routine analyses for all PAHs at E&P crude oil or condensate spill sites are unnecessary. However, naphthalene should be analyzed as part of an USEPA 8260 analysis along with the volatiles benzene, toluene, ethyl benzene, and xylenes.

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An Evaluation of Benzene Risk

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Introduction

Benzene is commonly found in the environment from both human activities and natural processes. Benzene was first discovered in 1825 and isolated from coal tar in 1849, while today it is manufactured mostly from petroleum sources. Benzene is used by industry to make other chemicals such as ethylbenzene for plastics manufacture, cumene for resins, and cyclohexane for nylon and synthetic fibers [1]. Natural sources of benzene in the environment include volcanoes, forest fires, and crude oil seeps. Benzene occurs naturally in most crude oils, is a byproduct of oil refining processes, and also occurs in natural gas production condensates.

Benzene is a known human carcinogen. In workers, long-term exposure to high concentrations of benzene in air has been shown to cause cancer of the blood-forming organs. In laboratory animals, benzene has been shown to produce several types of cancer following oral or inhalation exposure. There are still questions concerning both the mechanisms of benzene carcinogenesis and the most appropriate models for developing human risk estimates. These issues are actively being studied and debated in the scientific community. In addition to cancer, benzene is also known to produce other adverse health effects, again principally on the blood-forming organs, although neurological and reproductive effects may also be of concern [1]. Most people are exposed to a small amount of benzene every day, mainly via inhalation of vapors from commercial products such as glues, paints, cigarette smoke, and vehicle exhaust. People may come into contact with benzene through the inhalation, ingestion, or dermal contact exposure pathways.

Most upstream regulatory programs (such as those in the States of Texas and Louisiana) do not routinely require benzene analysis of exploration and production (E&P) site soils and do not routinely set regulatory limits for benzene in soil. Upstream regulatory agencies in California, New Mexico, and Michigan are exceptions and do require benzene analyses for soils at E&P sites. Regulatory limits for benzene in soil are routinely set in downstream regulatory programs, such as those with jurisdiction over underground storage tank (UST) sites. Most often, these are based on Tier 1 Risk Based Screening Levels (RBSLs) developed for protecting groundwater resources. In developing RBSLs, a number of fate and transport assumptions are typically used that are now known to be overly conservative for benzene. For example, Tier 1 RBSLs have

historically assumed that benzene in a complex mixture of petroleum hydrocarbons in soil behaves in the same way it would if it were the only chemical present in soil, and that there are no losses of benzene due to volatilization or biodegradation over time.

This study was conducted to improve the fate and transport assumptions typically used to derive RBSLs for benzene in soil. RBSLs are developed that take into consideration the attenuation of benzene in the vadose zone, as well as the presence of the complex petroleum mixture (expressed in terms of TPH) in soil. Additional attenuation of benzene in groundwater is not considered. The potential risk that benzene might pose at E&P sites is then evaluated by comparing these RBSLs to two estimates of potential benzene levels in E&P site soils. The first estimate is based on benzene levels found in several unweathered crude oils and condensates. The second is based on limited field data for actual benzene levels measured in E&P site soils following typical emergency response activities after spill events.

Benzene Concentrations in Crude Oils and Condensates

Sixty-nine unweathered crude oils and fourteen unweathered condensate samples were analyzed for volatile aromatic hydrocarbons, including benzene, toluene, ethylbenzene, and xylenes (BTEX) using purge and trap gas chromatography coupled with mass spectrometry (GC/MS). Samples were analyzed following a procedure based on the United States Environmental Protection Agency (USEPA) Method 8260A [2].

Figure 1 illustrates the sample locations for the 69 crude oils and 14 condensates. The American Petroleum Institute (API) gravity range for the crude oils in this study is 9 to 46°, and the range is 45 to 70° for the condensates. While all of the samples were analyzed for BTEX as discussed above, only the benzene values are presented here. Toluene, ethylbenzene, and xylenes (TEX) do not typically present a risk management concern at petroleum release sites. They are non-carcinogenic compounds and they are addressed as part of the petroleum mixture as a whole. TEX are included in the non-carcinogenic TPH RBSLs presented in Chapter 8. The analytical results for TEX are provided in Chapter 4.

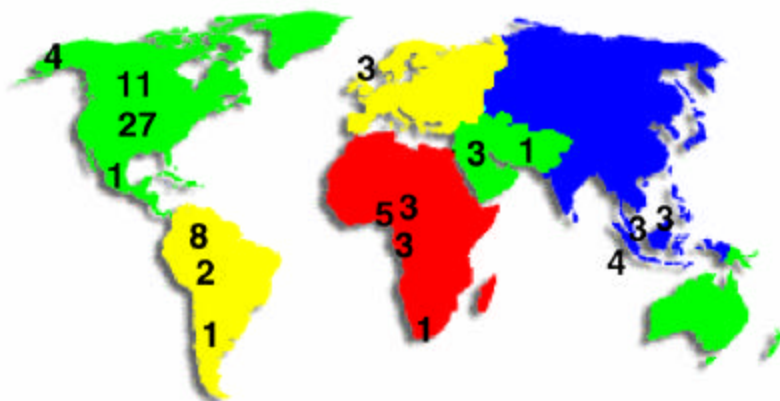


Figure 1. Sample locations for the crude oils and condensates. Twelve of the condensates were from the United States (excluding Alaska and Hawaii).

As shown in Table 1, the highest observed concentration of benzene in the 69 crude oils was 5900 mg/kg of oil or 0.59 wt %, and the mean concentration of benzene in the crude oils was 1,340 mg/kg. Two crude oils contained less than 1.2 mg/kg benzene (the detection limit for the analytical method). In general, higher API gravity crude oils and condensates tend to contain more benzene as shown in Figure 2. The condensates contained more benzene than the crude oils, with the maximum concentration being 35,600 mg/kg of condensate (3.56 wt %). The mean concentration of benzene for the 14 condensates was 10,300 mg/kg. There is roughly 10 times more benzene on average in the analyzed condensates than in the analyzed crude oils.

Table 1. Concentrations of benzene in crude oils and condensates analyzed in this study.

# of Samples	API Gravity Range (°)	Concentration of Benzene (mg/kg Oil)				Number of Samples With Benzene = ND
		Mean	Median	Minimum	Maximum	
69 Crude Oils	8.8–46.4	1,340	780	ND*	5900	2
14 Condensates	45–70.1	10,300	6400	1470	35,600	0

ND = Non-detect, with the sample detection limit = 0.32 mg benzene/kg oil.

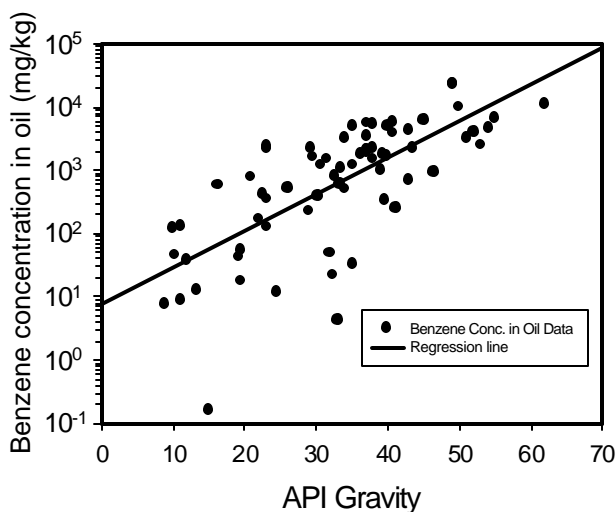


Figure 2. Benzene concentrations versus API gravity for 61 crude oils and 14 condensates (API gravity data were unavailable for 8 crude oils).

Benzene RBSLs for Groundwater Protection

Groundwater protection RBSLs for benzene in soil were developed for the scenario shown in Figure 3. In this scenario, a surface impoundment or a soil is impacted from a surface spill of oil (or condensate) in which the oil is confined to the unsaturated zone and does not reach groundwater, i.e., there is no free-phase oil at the water table. It is assumed that some response to the spill has already occurred and that the extent of contamination has been delineated such that the depth of contamination and level of contamination are known. The source of benzene contamination is confined to a layer of thickness, d , and the bottom of the contaminated layer is a distance, H , from the groundwater table.

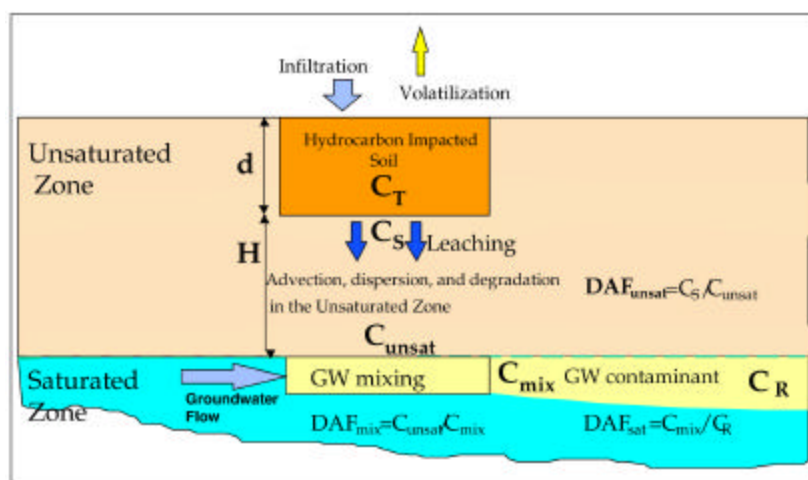


Figure 3. A conceptual site model showing a crude oil or condensate contaminated soil in the unsaturated zone and the various dilution and attenuation processes that occur during transport to groundwater.

In general, dilution and attenuation of benzene, or other chemicals, emanating from a source can occur in the unsaturated zone, a groundwater mixing zone, and in the groundwater downstream of the source. A typical RBSL calculation assumes an infinite source of the chemical of concern, which means there are no losses over time due to volatilization, leaching, or biodegradation in the hydrocarbon impacted layer. In addition, biodegradation in the zone between the bottom of the impacted soil and the groundwater table is not typically considered. These assumptions are overly conservative for benzene, because benzene is volatile and readily biodegradable, provided that oxygen does not limit the rate of biodegradation. Accordingly, the approach presented here for developing groundwater protection RBSLs for benzene in soil considers attenuation effects in the unsaturated zone, including a conservative accounting of degradation in the unsaturated zone between the bottom of the contaminated zone and the water table, as well as losses in the source of contamination due to volatilization and leaching. These are accounted for in an unsaturated zone dilution attenuation factor (DAF), DAF_{unsat} .

In addition to these attenuation considerations, the enhanced soil-water partitioning that occurs for benzene, due to the presence of a complex petroleum mixture in soil is also considered (i.e., the petroleum mixture keeps more of the benzene in the oily soil phase). Present approaches for calculating individual chemical RBSLs assume that partitioning occurs to native soil organic matter only.

The RBSL for benzene in soil that is protective of groundwater, $RBSL_{s-gw}$, was calculated using the following equation:

$$RBSL_{s-gw} = C_T = K_T * DAF_o * C_R \quad (1)$$

where:

C_T = The total concentration of benzene in soil based on the groundwater exposure pathway (g/g-soil)

C_R = The acceptable concentration of benzene in groundwater at the groundwater receptor (g/cm³-water)

C_R is either a risk-based screening level for water, $RBSL_w$, or a groundwater regulatory standard (in the United States, the maximum contaminant level for benzene in groundwater is 5×10^{-9} g/cm³-water; the State of New Mexico has a groundwater standard = 1.0×10^{-8} g/cm³-water).

If appropriate, $RBSL_w$ (g/cm³-w) can be calculated for benzene, a carcinogen, according to the following equation:

$$RBSL_w = \frac{TR * BW * AT_c * 365 * 10^{-6}}{IR_w * ED * EF * SF_o} \quad (2)$$

where:

TR = Target excess individual lifetime cancer risk (10^{-5})

BW = Adult body weight (70 kg)

AT_c = Averaging time for carcinogens (70 years)

SF_o = Oral cancer slope factor [mg/kg-day]⁻¹ (0.029 for benzene)

IR_w = Adult daily water ingestion rate (2 L/day)

EF = Exposure frequency for residents (350 days/year)

ED = Exposure duration for adult residents (30 years)

K_T = The total partition coefficient for benzene. It is the ratio of total soil concentration to pore water concentration in the source zone of the contamination (cm³-water/g-soil).

DAF_o = The overall dilution attenuation factor (unitless) which is defined as:

$$DAF_o = DAF_{unsat} * DAF_{mix} * DAF_{sat} \quad (3)$$

where:

DAF_{unsat} = C_s/C_{unsat} = Unsaturated zone dilution attenuation factor (unitless)

- $DAF_{mix} = C_{unsat}/C_{mix}$ = Groundwater mixing zone dilution attenuation factor (unitless)
 $DAF_{sat} = C_{mix}/C_R$ = Dilution attenuation factor in groundwater downstream of the source (unitless)
 C_s = Concentration in pore water at the source of contamination (g/cm^3 -w)
 C_{unsat} = Concentration in pore water at the bottom of the unsaturated zone (g/cm^3 -w)
 C_{mix} = Concentration in groundwater at the downstream edge of the mixing zone (g/cm^3 -w)

Equations for determining the overall soil-water partition coefficient and the various DAFs are presented in the paragraphs below.

Soil-Water Partition Coefficient, K_T

The overall soil-water partition coefficient, K_T , is given by:

$$K_T = \frac{C_T}{C_s} = \frac{q_w + K_o r_b + K_a q_a + K_o q_o}{r_b} \quad (4)$$

where:

- C_T = Total concentration of chemical in soil (g/g soil)
 C_s = Concentration in pore water at the source of contamination (g/cm^3 -w)
 ρ_b = Soil bulk density (g -soil/ cm^3 -soil)
 θ_w = Volumetric water content in vadose zone soils (cm^3 -w/ cm^3 -soil)
 K_d = Soil-water sorption coefficient for chemical (cm^3 -w/ g -soil)
 K_a = Air-water partition coefficient (dimensionless Henry's Law constant) for chemical (cm^3 -w/ cm^3 -air)
 θ_a = Volumetric air content in vadose zone soils (cm^3 -air/ cm^3 -soil)
 K_o = Oil-water partition coefficient (cm^3 -w/ cm^3 -oil)
 θ_o = Volumetric oil content in vadose zone soils (cm^3 -air/ cm^3 -soil)

Note that in Equation (4) partitioning of the chemical to residually trapped oil in the soil is included. This represents additional partitioning that occurs when a residual oil phase is present. Thus the levels of benzene that are acceptable in the soil depend on the oil content in the soil. The oil-water partition coefficient can be determined from Raoult's Law [3,4,5] as:

$$K_o = \frac{r_o MW_i}{S_i MW_o} \quad (5)$$

where:

ρ_o = Density of oil phase (g-o/cm³-o)
 MW_i = Molecular weight of contaminant (g-/mole)
 MW_o = Molecular weight of oil phase (g -o/mole)
 S_i = Solubility of pure chemical in water (g-/cm³-w)

The volumetric oil content in the soil can be related to the residual TPH concentration with the following equation:

$$q_o = \frac{r_b C_{TPH}}{r_o} \quad (6)$$

where:

C_{TPH} = Residually trapped TPH concentration in soil (g/g-soil)

Substituting Equations (5) and (6) for $K_o\theta_o$, Equation (4) becomes:

$$K_T = \frac{q_w + K_d r_b + K_a q_a + \frac{r_b MW_i C_{TPH}}{S_i MW_o}}{r_b} \quad (7)$$

Thus, the overall partition coefficient, K_T , will be dependent upon the level of residual TPH in the soil. (Note that the residual TPH level is the amount in excess of the sorbed TPH level which is nominally <100 mg/kg for a low organic carbon content soil.)

Summary of DAF_{unsat}

The attenuation in the unsaturated zone is due to the following factors:

- 1) Biodegradation of the contaminant in the region beneath the source of contamination and the groundwater table.
- 2) Depletion of the concentrations in the source of contamination due to losses associated with leaching, volatilization, and biodegradation.

A commonly used approach for modeling vadose zone transport is that of Ünli et al. [6] which uses the equation of van Genuchten and Alves [7]. This equation is also the basis for modeling unsaturated zone transport in the computer model VADSAT [6]. To determine DAF_{unsat} values for the RBSLs presented here a simpler model was used. This model is based on treating the contaminated zone and the unsaturated zone beneath the contaminated zone (see Figure 3) as two separate, completely mixed zones. (The Ünli model treats the

source zone as a completely mixed zone, but models advection and dispersion in the region below the source zone.) This completely-mixed model approach was used here because it is computationally easy to use (it is possible to develop a simple algebraic expression for DAF_{unsat}) and retains the essential parameters of the Ünlü et al. model. For completely-mixed conditions, the DAF_{unsat} can be determined from the following equation:

$$DAF_{unsat} = \frac{H r_b K_{T,unsat}}{u} \frac{a - b}{\left(\frac{a}{b}\right)^{\frac{b}{b-a}} - \left(\frac{a}{b}\right)^{\frac{a}{b-a}}} \quad (8)$$

where:

$$a = \frac{\frac{u}{H} + I_{unsat}}{r_b K_{T,unsat}} \quad (9)$$

and

$$b = \frac{I_v + \frac{u}{d} + I_s}{r_b K_{T,S}} \quad (10)$$

DAF_{unsat} in Equation 8 is equal to the ratio $C_{so}/C_{unsat, max}$ where:

- C_{so} = The initial concentration in the pore water at the source of contamination (g/cm^3 -w)
- $C_{unsat, max}$ = Maximum pore water concentration at the bottom of the unsaturated zone (g/cm^3 -w)

The parameter α (day^{-1}) represents the effect of biodegradation in the unsaturated zone on DAF_{unsat} and the parameter β (day^{-1}) represents the effect of the various source losses on DAF_{unsat} . The following parameters that make up α and β are:

- u = The infiltration rate (cm/day)
- H = Distance from the bottom of the contaminated source region to the water table (cm)
- d = Depth of the source of contamination (cm)
- λ_{unsat} = Degradation constant in unsaturated zone beneath the source zone (day^{-1})
- λ_s = Degradation constant in the source zone (day^{-1})

- $K_{T,unsat}$ = The overall soil-water partition coefficient for the unsaturated zone (cm³-water/g-soil)
 $K_{T,S}$ = The overall soil-water partition coefficient for the source zone (cm³-water/g-soil)
 λ_w = Volatilization rate constant for the source zone (day⁻¹)
 ρ_b = Bulk density of the soil (g-soil/cm³-soil)

The volatilization rate constant, λ_w , can be estimated from:

$$I_V = \frac{p^2 D_{wT,S}}{4d^2} \quad (11)$$

where:

$D_{wT,S}$ = Total effective diffusion coefficient defined in terms of a chemical's concentration gradient in water (cm²/day)

$D_{wT,S}$ is defined mathematically as:

$$D_{wT,S} = D_{w,eff} + K_a D_{a,eff} + K_o D_{o,eff} \quad (12)$$

The effective diffusion coefficients were determined as follows [8]:

$$D_{w,eff} = D_{wm} \frac{q_w^{3.33}}{f^2}; \quad D_{a,eff} = D_{am} \frac{q_a^{3.33}}{f^2}; \quad \text{and} \quad D_{o,eff} = D_{om} \frac{q_o^{3.33}}{f^2} \quad (13)$$

where D_{wm} , D_{am} , and D_{om} are the molecular diffusion coefficients (cm²/sec) of the given chemical in the water, air, and residual oil phases, respectively. The following values were used for benzene: $D_{wm} = 1.10\text{E-}05$ cm²/sec [9], $D_{am} = 0.093$ cm²/sec [9], $D_{om} = 3.4\text{E-}05$ cm²/sec [10]. In general, the contribution of the oil phase diffusion term to $D_{wT,S}$ was not significant.

The expression for the first order volatilization rate constant, λ_w , was determined from the solution for transient diffusion at long times from a slab of thickness, d , with a pore water concentration equal to zero at the top surface and zero flux at the bottom surface [11]. We have therefore assumed that there is no additional resistance to mass transfer at the soil-air interface. The boundary layer mass transfer resistance will be small relative to the diffusion resistance in the soil, so it is reasonable to neglect this resistance. If an overburden layer exists, then its thickness can be added to the parameter d in Equation 11. This assumes that the overburden properties are similar to the source region. This would be a conservative assumption with respect to source depletion, since the partitioning

would be lower in the overburden layer than in the source region due to the presence of residual hydrocarbon in the source versus the overburden layer.

Biodegradation of benzene in subsurface soils can be limited by the mass transfer of oxygen. As a result, the first step in evaluating attenuation of benzene due to degradation was to determine whether there would be sufficient oxygen present from the bottom of the contaminated source region downward through the unsaturated zone to the groundwater table. When oxygen concentrations are above a threshold concentration, then a conservative first order reaction rate constant can be used to estimate the attenuation of benzene in the unsaturated zone. In developing the benzene RBSLs, a conservative first order pore water-based biodegradation rate constant = 0.01 day^{-1} was assumed when the source thickness was less than a critical value.¹ For a sandy soil this critical source thickness was estimated to be $d \cong 5 \text{ ft}$ (calculations are not presented here). A pore water-based biodegradation rate constant = 0.01 day^{-1} translates to a soil based degradation constant, $\lambda_{\text{unsat}} = 0.00094 \text{ day}^{-1}$ for a sandy soil with a volumetric water content, $\theta_w = 0.094 \text{ cm}^3\text{-w/cm}^3\text{-soil}$.

Note that Equation (8) assumes that the $\text{DAF}_{\text{unsat}}$ is based on the maximum aqueous concentration that will reach the groundwater table. It is therefore conservative, since the average concentration in water observed over a typical exposure period would be significantly lower.

Summary of DAF_{mix}

The DAF in the mixing zone can be determined from the following equation:

$$\text{DAF}_{\text{mix}} = 1 + \frac{U_{\text{gw}} d_{\text{gw}}}{IL} \quad (14)$$

where:

U_{gw} = Groundwater Darcy velocity (cm/year)

I = Infiltration rate of water through soil (cm/year)

L = Length of source area parallel to groundwater flow direction (cm)

¹ A review of aerobic degradation studies of benzene inferred 1st order degradation rate constants ranging from $0.02\text{-}2 \text{ day}^{-1}$ for high benzene concentrations, i.e., 100 mg/L [12]. These rate constants were based on water phase concentrations and were obtained from a review of several laboratory microcosm and column studies and some field measurements for which hydrocarbon and oxygen concentration profiles in the unsaturated zone were determined. Apparent 1st order degradation constants will be higher than these values for lower benzene pore water concentrations [12].

δ_{gw} = Groundwater mixing zone thickness (cm)

A DAF_{mix} value = 8.7 was used to calculate benzene RBSLs. This is the value used in the recently developed New Mexico UST Guidelines for Corrective Action [9]. For comparison, using the ASTM [13,14] default parameters for U_{gw} , I , L , and δ_{gw} yields a DAF_{mix} = 12.1.

Summary of DAF_{sat}

A DAF_{sat} value = 1 has been assumed which is equivalent to no attenuation downstream of the source due to dispersion and degradation. This would be valid if the receptor is located at the downstream edge of the source. If the receptor is located some distance away from the source, DAF_{sat} will increase because of dispersion and biodegradation of the chemical in groundwater. Values of DAF_{sat} developed for a recently developed soil screening guidance program are shown in Table 2. Biodegradation in groundwater was neglected for the values shown in Table 2. Accounting for the typical biodegradation rates for benzene that occur in groundwater will result in higher DAF_{sat} values than those shown in Table 2. Equations such as that of Domenico [15] with appropriate soil and chemical parameters can be used for calculating screening level estimates of DAF_{sat} .

Table 2. Dilution Attenuation Factors (DAF_{sat}) (1).

Distance From Edge of Mixing Zone (Ft)	DAF_{sat} (Without Degradation)
0	1.0
50	1.1
100	2.2
150	4.2
250	11
500	41
1000	163

- 1) From Table 4-14, New Mexico Environmental Department Guidelines for Corrective Action [9].

Benzene RBSL_{s-gw} Curves

Benzene RBSL_{s-gw} were calculated using the equations described above for several values of TPH, H (distance from the bottom of the contaminated source zone to the water table) and a constant value of d (thickness of the contaminated source zone). No degradation in the groundwater (saturated zone) downstream of the source area was included in these calculations. If degradation were

included (meaning $DAF_{\text{sat}} > 1$), the RBSLs would be greater than those shown in Figure 4.

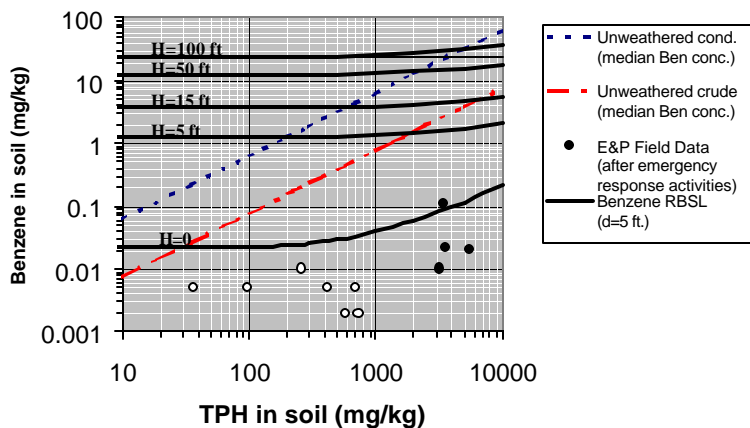


Figure 4. Comparison of soil RBSLs for benzene with a) predicted soil levels for unweathered crude oils and condensates and b) actual soil levels after emergency response activities at a few E&P sites. Open (white) symbols represent detection levels for benzene. Soil RBSLs for benzene are for the groundwater exposure pathway. Calculations were based on a sandy soil type and include vadose zone attenuation due to volatilization and leaching from the source and biodegradation beneath the source (see Figure 3). H = the distance from the bottom of the contaminated soil zone to the groundwater table.

The calculation of RBSLs considers the following important factors: 1) degradation in the unsaturated zone between the source of contamination and the groundwater table, 2) source losses due to volatilization and leaching, and 3) enhanced partitioning of benzene in soils due to the presence of TPH. Parameters that determine the relative importance of these factors include the depth to groundwater, the thickness of the source of contamination, and the soil type. All of these three factors significantly contribute to higher acceptable levels of benzene in soil than would be acceptable if attenuation and increased partitioning in the vadose zone were not considered.

The RBSL curves presented in Figure 4 are based on a sandy soil type; a biodegradation constant, $\lambda_{\text{unsat}} = 9.4\text{E-}04 \text{ day}^{-1}$; a hydrocarbon impacted layer of thickness, $d=5 \text{ ft}$; and a groundwater standard = 0.010 mg/L . Values of other parameters for determining the curves in Figure 4 are listed in Table 3.

Table 3. Parameters used for benzene DAF_{unsat} and $RBSL_{s-gw}$ calculations.

Soil or Contaminant Parameter	Source Layer (1)	Unsaturated Zone Layer Beneath Source
u (cm/yr)	20	20
ϕ (cm^3 -pores/ cm^3 -soil)	0.349(2)	0.349(2)
θ_w (cm^3 -w/ cm^3 -soil)	0.094(3)	0.094(3)
θ_o (cm^3 -o/ cm^3 -soil)	0.019(1)	0.0
θ_a (cm^3 -a/ cm^3 -soil)	0.236(1)	0.255
D_{wm} (cm^2 /sec)	1.10E-05	1.10E-05
D_{am} (cm^2 /sec)	0.093	0.093
D_{om} (cm^2 /sec)	3.40E-05	-
K_a (cm^3 -w/ cm^3 -a)	2.20E-01	2.20E-01
K_o (cm^3 -w/ cm^3 -o)	2.01E+02	-
f_{oc} (g oc/g soil)	2.00E-03	2.00E-03
K_{oc} (cm^3 -w/g oc)	83	83
ρ_b (g soil/ cm^3 soil)	1.73(2)	1.73(2)
ρ_o (g oil/ cm^3 oil)	0.90	-
$D_{wT,S}$ (cm^2 /sec)	1.36E-03(1)	-
$K_{T,S}$ (cm^3 -w/g soil)	2.47(1)	-
$K_{T,unsat}$ (cm^3 -w/g soil)	-	0.252
MW_i	78	78
MW_o	200	-
λ_s (day ⁻¹)	0	-
λ_{unsat} (day ⁻¹)	-	9.4E-04
d (ft)	5	-

- 1) Values shown are for TPH = 10,000 mg/kg-soil.
- 2) From Brakensiek et al. [16].
- 3) Determined from $u = 20$ cm/yr and Brooks-Cory parameters from Brakensiek et al. [16] and saturated hydraulic conductivities from Carsel and Parrish [17].

In Figure 4 RBSLs are shown for benzene as a function of TPH in the soil and for distance to groundwater, H . The following key points can be made regarding this figure:

Effect of TPH on Benzene $RBSL_{s-gw}$

The presence of TPH increases the benzene RBSL due to increased partitioning. At short depths to groundwater, the presence of TPH has the greatest effect on the RBSL. When only the sorption of benzene to soil particles is considered (TPH <100 mg/kg), for $H = 0$ the RBSL = 0.022 mg/kg. A level of TPH of

10,000 mg/kg results in an increase in the RBSL to 0.21 mg/kg. There is less effect of TPH on RBSLs at greater depths, H , because higher TPH levels result in relatively less attenuation from source losses.

Effect of Depth to Groundwater, H , on Benzene $RBSL_{s-gw}$

When $H = 0$, there is no attenuation in the unsaturated zone ($DAF_{unsat} = 1$). As H increases, attenuation occurs between the bottom of the contaminated zone and the groundwater table. This is a result of degradation over depth H and of losses due to volatilization and leaching in the hydrocarbon impacted layer of thickness, d . As H increases, attenuation increases, and the RBSL increases. For $d=5$ ft, the increase in RBSL is due to increased degradation with contributions from losses due to volatilization and leaching in the contaminated region.

Benzene RBSLs for Surface Soil Exposure

Benzene RBSLs for exposure of commercial workers to surficial soils via the pathways of ingestion, inhalation of vapors and particulates, and dermal contact ($RBSL_{ss}$) were also determined for comparison with the groundwater based $RBSL_{s-gw}$ values and are shown in Table 4. Methods for determining $RBSL_{ss}$ were consistent with ASTM E1739-95 and E2081-00 guidelines [13,14].

Table 4. Benzene risk-based soil screening levels for exposure of a commercial worker to surficial soil (1).

Thickness of Impacted Layer, d (Ft)	$RBSL_{ss}$ (mg/kg Soil)
2	484
5	290
10	174

- 1) Surficial soil pathways include: ingestion, inhalation (vapor emission and particulates), and dermal contact.

The $RBSL_{ss}$ values in Table 4 increase as the thickness of the impacted layer (d) decreases, because a smaller thickness (d) results in a lower exposure to benzene. These $RBSL_{ss}$ values are greater than the benzene soil RBSL values shown in Figure 4 based on the groundwater exposure pathway ($RBSL_{s-gw}$). This indicates that groundwater protection is likely to be the major risk management concern for benzene at most sites.

Comparison of RBSLs With Expected Benzene Levels at E&P Sites

Figure 4 also presents lines for predicted benzene soil levels that would correspond to varying levels of E&P site contamination by unweathered condensates and crude oils. The lines are based on the median concentrations of benzene observed for the 69 crude oils and the 14 condensates for which composition data were summarized in Table 1. Figure 4 also presents field data from various E&P sites for benzene soil concentrations, plotted versus the corresponding TPH soil levels for these sites. Most of these data are from sites impacted by crude oils, but data from a few condensate impacted sites are also included. For these sites, soil samples were obtained soon after emergency response activities were completed.

Comparisons of the E&P field data with the unweathered crude oil and condensate data indicate that typical emergency response activities significantly reduce the levels of benzene in soils. Figure 4 also indicates that sites impacted by condensates and crude oils may not exceed benzene groundwater standards even for short distances to the water table (H). However, benzene soil levels that correspond to unweathered crude oils and especially to unweathered condensates, may present a risk to groundwater at certain TPH levels and depths to groundwater. It should be noted that the benzene RBSLs presented in this chapter do not account for attenuation in the saturated zone, which can be significant when the point of compliance is downstream of the source.

Summary

An improved approach to developing RBSLs for benzene in soil that are protective of groundwater was developed that makes use of more realistic fate and transport assumptions than are typically used in most Tier 1 calculations. Attenuation effects were considered, including a conservative accounting of minimal biodegradation in the unsaturated zone between the bottom of the contaminated zone and the water table, as well as losses in the source of contamination due to volatilization and leaching. In addition to these attenuation considerations, the enhanced soil-water partitioning that occurs for benzene due to the presence of TPH in soil was also considered. All of these factors significantly contribute to higher acceptable levels of benzene in soil than would be estimated if attenuation and increased partitioning in the vadose zone were not considered. Additional attenuation in the saturated zone was not considered but would further increase acceptable levels of benzene in some cases.

Benzene RBSLs were found to depend on some key parameters: 1) depth to groundwater (H), 2) thickness of oil impacted layer (d), and 3) level of TPH in the soil. These parameters determine the amount of attenuation of benzene in

the vadose zone and the decreased partitioning of benzene to soil when TPH is present. An easy to use figure was presented that can be used to select the appropriate benzene RBSL for an individual site if the above factors are known. This figure illustrates that RBSLs increase by a factor of 10 to 1000 when vadose zone attenuation and increased partitioning (water to soil) due to TPH are taken into account.

The potential risk posed by benzene at E&P sites was also evaluated. Overall, the major risk management concern for benzene at most E&P sites is likely to be due to its potential to impact groundwater and not due to direct commercial worker exposure to impacted surface soils. Benzene may present a risk to groundwater at some E&P sites. The potential risk will depend on the type of oil (crude oil or condensate) spilled, the depth to groundwater, the thickness of contamination, the level of TPH in the soil, and the extent of weathering of benzene from soils that results from any emergency response activities.

The benzene RBSLs presented in this chapter are illustrative of screening levels that could be used in conjunction with TPH RBSLs to decide if further corrective action is required at a given site. To use screening levels such as these for benzene it is assumed that some response to a spill has already occurred and that the extent of contamination has been delineated such that the depth of contamination and level of contamination of benzene and TPH are known.

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Risk Evaluation of Metals in Crude Oils

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Introduction

Metals and semi-metals are commonly found in the environment (hereafter metals and semi-metals are simply referred to as “metals”). They are present in the rocks, soil, and organic matter that are the building blocks for the earth. Some metals (such as chromium, selenium, and zinc) are essential to life and must be supplemented as trace elements in the diets of humans and animals. However, adverse health effects may be produced in people or other environmental receptors when they are exposed to metals at certain concentrations and under certain exposure conditions. For example, millions of people inhabiting regions having iodine-deficient soils in eastern Africa are susceptible to goiter, while Itai-Itai disease in China is attributed to people living in areas where soils are contaminated by cadmium-containing wastes [1]. Some metals, such as arsenic, cadmium, chromium, and nickel, have been shown to produce cancer in people under some exposure conditions. Some metals have been shown to produce adverse reproductive and/or other types of health effects in people (e.g., lead, cadmium, mercury) and other animals (e.g., mercury, selenium).

The chemical species of a metal is important in determining a metal's toxicity. For example, the inorganic form of arsenic is believed to be the carcinogenic form, while the organic forms are not. Also, hexavalent chromium is carcinogenic, while trivalent and elemental chromium are not. Therefore, knowledge of the specific form of metal in an environmental sample (such as an oil, waste, or soil sample) is important for accurate risk evaluation. Although it is well known that different chemical forms of the same metal have different toxicities, the analytical methodologies commonly employed do not readily distinguish between different metal species. As a result, risk evaluations for metals are usually based on the very conservative assumption that any metal detected in a sample is in a form that may produce toxicity. This assumption results in an overestimation of the potential risks posed by metals in environmental samples.

Metals are natural components of crude oil. The chlorophyll molecule in decomposing vegetative matter loses magnesium during crude oil formation, and the magnesium is replaced by vanadium or nickel. The amount of vanadium and

nickel in crude oils is well documented and their relative abundance can be used to identify the source and age of crude oils [2]. However, there is little published information on other metals in crude oils that may be of concern to human health and the environment.

In contrast, the metals content of drilling muds has been investigated by the United States Environmental Protection Agency (USEPA) [3]. Drilling muds contain elevated levels of some specific metals such as barium. The American Petroleum Institute (API) has also analyzed drilling muds and other exploration and production (E&P) wastes (e.g., tank bottoms and produced sand) for metals [4].

Through a joint industry research project carried out by the Petroleum Environmental Research Forum, a more thorough understanding of the types and concentrations of metals in crude oil was gained. The identification of particular species of metals in crude oils was not attempted. Commonly employed analytical methodologies were used, and it was then assumed that the metals detected were in a form that may produce toxicity for risk evaluation purposes, consistent with standard risk assessment practice. Therefore, as discussed above, the risk evaluation for the metals detected in this study is conservative. The technical information obtained in this study is needed by regulators, risk assessors, and site managers to implement risk-based decisions at sites that have been impacted by crude oil.

The Current Status of Metals Regulations & Risk Assessment

The State of Louisiana is currently the only state within the United States that routinely requires the analysis of metals in E&P wastes. The La29B regulatory limits for metals are provided in Table 1 [5]. These regulatory limits are not risk-based values. In 1995, the API developed risk-based guidance levels for metals to be used in the land management of E&P wastes based upon the assumptions and calculations developed by the USEPA for land application of sewage sludge [6,7]. Both API and USEPA evaluated 14 different exposure pathways of concern for ecological and human health. The API's maximum soil concentrations for 11 of the 18 metals analyzed in this study are shown in Table 1. However, to date, no state regulatory agency in the United States has adopted the API metals guidance as regulatory criteria. In the absence of specific regulations for metals, comparison of metals concentrations to the API criteria or to Louisiana's regulatory levels may be useful.

In some cases, a risk assessment of metals has been required by local regulators to determine whether metals in soil impacted by crude oil might pose a risk to human health or the environment. This can be very difficult to do because it is often impossible to conclusively differentiate metals that may be naturally

present in soils from those that may have originated from a crude oil spill, or from other sources.

The USEPA and many state agencies have developed human health risk-based screening levels for metals. These screening levels are not regulatory limits, but are commonly used as Tier 1 screening tools for evaluating risks, as described in Chapter 1. The USEPA has developed Preliminary Remediation Goals (PRGs) [8] for evaluating potential human health effects at Superfund sites. The PRGs for metals are provided in Table 1. As an example of a state regulatory program, the Texas Natural Resource Conservation Commission (TNRCC) has developed Protective Concentration Levels (PCLs) under the Texas Risk Reduction Program (TRRP) and the lowest residential PCLs for all exposure pathways are also listed in Table 1 [9].

PRGs and PCLs represent chemical concentrations in environmental media (soil, water, and air) that are considered protective of humans, including sensitive groups, over a lifetime of exposure. They can be used to evaluate potential health risks, trigger further site investigation, and serve as initial remediation goals. Chemical concentrations above PRGs or PCLs do not automatically mean that a site must be cleaned up to ensure public health, but they do suggest that further evaluation of the potential risks posed by site contaminants may be in order.

The PRGs presented in Table 1 are based on human exposure pathways involving direct contact with contaminated soil and they focus on incidental ingestion, dermal contact, and inhalation of vapors or soil particles containing the chemicals of concern. They are derived by combining current USEPA toxicity values with “standard” exposure factors and they correspond to fixed levels of risk [i.e., either a one-in-one million (1×10^{-6}) cancer risk or a non-carcinogenic hazard quotient of one], depending upon the risk levels selected by the regulatory agency. The Texas PCLs are based on the same direct contact exposure pathways, but they include additional indirect exposure pathways such as potential leaching to groundwater and uptake into garden vegetables grown in residential surface soil. They correspond to a target cancer risk level of one-in-one-hundred thousand (1×10^{-5}) and a non-carcinogenic hazard quotient of one. For antimony, barium, beryllium, cadmium, chromium (total), lead, selenium, and thallium, the lowest residential PCL is based on the metal leaching to groundwater. PCLs for direct human contact with impacted soil are higher than the levels presented.

Table 1. Comparison of regulatory limits, PRGs, miscellaneous guidance levels, and mean concentrations of metals in soils of the United States (U.S.).

	La29B (mg/kg)	USEPA Region IX PRG (mg/kg)		Texas Lowest Residential PCL (mg/kg)	API Guidance Level (mg/kg)	Lowest Ecological SSL ⁶ (mg/kg)	Mean U.S. Soil Conc. [10] (mg/kg)	
		Residential	Industrial					
Ag (Silver)	NA	390	10,000	0.48	NA	2	ORNL-P	ND
As (Arsenic)	10	0.39	2.7	24	41	10	ORNL-P	5.2
Ba (Barium)	20,000 ^{1a} 40,000 ^{1b} 100,000 ^{1c}	5,400	100,000 ⁷	440	180,000	500	ORNL-P	440
Be (Beryllium)	NA	150	2,200	1.8	NA	4	CCME-A	0.63
Cd (Cadmium)	10	37	810	1.5	26	3	CCME-A	ND
Co (Cobalt)	NA	4,700	100,000 ⁷	1,300	NA	20	ORNL-P	6.7
Cr (Chromium (Total))	500	210 ³	450 ³	2,400	1500 ³	0.4	ORNL-E	37
Cu (Copper)	NA	2,900	76,000	550	750	60	ORNL-E	17
Hg (Mercury)	10	23	610	2.1	17	0.1	ORNL-E	0.058
Mo (Molybdenum)	NA	390	10,000	49	37 ⁴	2	ORNL-P	0.59
Ni (Nickel)	NA	1,600	41,000	160	210	30	ORNL-P	13
Pb (Lead)	500	400	750	3	300	50	ORNL-P	16
Sb (Antimony)	NA	31	820	5.4	NA	5	ORNL-P	0.48
Se (Selenium)	10	390	10,000	2.3	100 ⁵	1	ORNL-P	0.26
Sn (Tin)	NA	47,000	100,000 ⁷	35,000	NA	2	CCME-A	.89
Tl (Thallium)	NA	5.2	130	1.7	NA	1	ORNL-P CCME-A	ND
V (Vanadium)	NA	550	14,000	290	NA	2	ORNL-P	58
Zn (Zinc)	500	23,000	100,000 ⁷	2,400	1400	50	ORNL-P	48

PRG = Preliminary Remediation Goal

PCL = Protective Concentration Level from Texas Risk Reduction Program

NA = Not Available

- 1) Louisiana 29B values for (a) wetlands, (b) uplands, and (c) commercial landfarming facilities.
- 2) A hot water soluble method for extraction of boron is recommended (Carter, 1993, "Soil Sampling and Methods of Analysis, Boca Raton," Lewis Publishers, pp 91-94). The guidance for boron is based on the soluble concentration with units of mg/L rather than the total concentration (mg/kg).
- 3) The chromium value given in the USEPA PRGs is based on a combination of chromium (VI) and chromium (III), while the API assumed that all chromium in soil would be chromium (III).
- 4) Under certain conditions this level of molybdenum may not be protective of grazing livestock. These conditions are alkaline soils under arid and semi-arid conditions with deficient levels of copper in the soil.
- 5) The potential for plant uptake of selenium may be high in alkaline soils under arid or semi-arid conditions. Plants that accumulate selenium in such soils may pose a threat to grazing animals. If elevated levels of selenium are found in the waste, safeguards should be taken to limit this exposure pathway.
- 6) Sources of lowest ecological benchmarks are: ORNL-P = screening benchmark to protect terrestrial plants [12]; CCME-A = CCME remediation criteria for agricultural land-use [13]; ORNL-E = screening benchmark to protect earthworms [11].
- 7) PRGs for relatively less toxic inorganic contaminants are set at a ceiling limit of 100,000 mg/kg. These values are not risk-based and represent a USEPA Region IX policy decision. Health risk-based PRGs for these metals would be higher than 100,000 mg/kg.

Ecological soil screening levels (SSLs), or benchmarks, have been developed by groups in North America and Europe. Ecological SSLs are chemical concentrations in soil below which it is unlikely that the chemical of potential concern would pose an unacceptable risk to ecological receptors. These may be considered Tier 1 screening levels to be used for evaluating potential risks to environmental receptors. As with human health-based PRGs and PCLs, chemical concentrations above ecological SSLs do not mean that a site must be

cleaned up, but they do suggest that the chemical(s) should be further evaluated in an ecological risk assessment.

Ecological SSLs may be specific to a particular type of ecological receptor such as plants, invertebrates, or microbial communities, and they may be specific to a particular type of land use. The lowest ecological benchmarks available from published sources are shown in Table 1. Sources for ecological soil benchmarks include the Oak Ridge National Laboratory (ORNL) soil benchmarks for soil and litter invertebrates (e.g., earthworms), heterotrophic soil microbial communities, and terrestrial plants [11,12]; Canadian Council of Ministers of the Environment (CCME) remediation criteria for agricultural land-use [13]; and the Dutch National Institute of Public Health and the Environment (RIVM) Ecotoxicological Intervention values [14]. Note that ecological SSLs have not been developed for specific hydrocarbons in soil (e.g., benzene and naphthalene); however, some have been developed for hydrocarbon fractions of a Canadian crude oil [15].

In any risk evaluation for metals, it is critical to consider the background levels of metals in soils. A thorough investigation of the concentrations of metals in uncontaminated background soils in the United States has been reported by the United States Geological Survey [10]. The mean values reported for metals in soils in the United States from this publication are also provided in Table 1.

Laboratory Procedures Used to Measure Metal Concentrations in Crude Oils

Twenty-six crude oils were analyzed for 18 metals that may pose a risk to human health or the environment. The metals concentrations of the crude oils are provided in Table 2. Figure 1 illustrates the geographic locations from which the crude oil samples were obtained. The metals contents were determined by Florida Institute of Technology researchers, as described below.

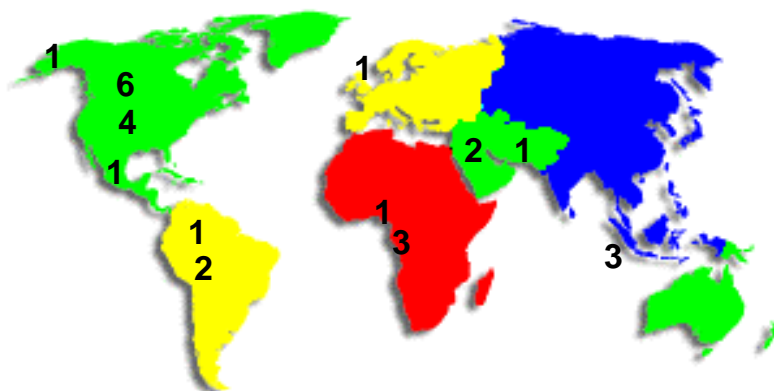


Figure 1. Number of crude oil samples (26 total) analyzed by the geographic region from which they originated.

For all metals except mercury and selenium, a 1-gram aliquot of each crude oil was weighed into a glass digestion flask and sealed with a glass watch cover. The samples were moved to hotplates and then digested with concentrated, high-purity sulfuric acid (H_2SO_4), nitric acid (HNO_3), and hydrogen peroxide. A separate digestion was performed for selenium, with 1-gram subsamples of each crude oil and high-purity HNO_3 as the only oxidizing acid. For mercury determinations, a 0.1-gram subsample of each crude oil was weighed into a glass digestion tube and oxidized with concentrated, high-purity HNO_3 and H_2SO_4 . Once the crude oil digestions were completed, the samples were placed in graduated cylinders, diluted to 10 mL with reagent water rinses of the digestion tubes, and stored for analysis in 15 mL polyethylene bottles.

Crude oil Standard Reference Materials (SRMs) with trace metal concentrations certified at environmental levels do not exist; therefore, additional crude oil subsamples were weighed and then spiked with the elements of interest. Acid digestion was selected for crude oil decomposition rather than ashing techniques for two reasons: (1) the lower temperatures used during acid digestion were less likely to cause the loss of volatile elements, and (2) the risk of sample contamination was less.

Metal concentrations of the digested crude oil samples, spiked samples, and blanks were determined by one of four methods: flame atomic absorption spectrometry (FAAS), graphite furnace atomic absorption spectrometry (GFAAS), inductively coupled plasma-mass spectrometry (ICP-MS), or cold-vapor atomic absorption spectrometry (CVAAS). Concentrations of zinc (Zn) were measured by FAAS using a Perkin-Elmer Model 4000 AAS. Cadmium

(Cd), cobalt (Co), chromium (Cr), copper (Cu), molybdenum (Mo), nickel (Ni), and vanadium (V) concentrations were determined by GFAAS with a Perkin-Elmer Model 4000 AAS utilizing a HGA-400 graphite furnace and AS-40 autosampler. A Perkin-Elmer Model 5100 AAS with HGA-600 graphite furnace and AS-60 autosampler was used to measure concentrations of silver (Ag), arsenic (As), beryllium (Be), and selenium (Se) by GFAAS. Concentrations of barium (Ba), lead (Pb), antimony (Sb), tin (Sn), and thallium (Tl) were measured by ICP-MS using a Perkin-Elmer ELAN 5000 spectrometer. Crude oil mercury (Hg) concentrations were determined by CVAAS using a Laboratory Data Control Model 1235 Mercury Monitor.

Results: Metals Concentrations in Crude Oils

The concentrations of metals in each crude oil tested are presented in Table 2. A summary of the data, including the method detection limits, is provided in Table 3. The method detection limits for the metals were 6 to 1,000 times lower than the suggested USEPA reporting limit for soils.

Table 2. Amount of metals in crude oils (data are in mg/kg oil).

	API Gravity	Ag	As	Ba	Be	Cd	Co	Cr	Cu	Hg
Africa #1	35.0	0.07	0.19	ND	ND	0.006	0.44	0.035	0.031	ND
Africa #2	37.1	0.11	ND	ND	ND	0.003	ND	0.021	0.023	ND
Africa #3	37.8	0.15	ND	ND	ND	0.014	ND	0.369	0.058	ND
Africa #4	33.3	0.09	ND	0.054	ND	0.026	0.38	0.124	0.083	ND
Asia	46.4	0.11	ND	0.032	ND	0.016	ND	0.067	0.069	ND
Central America	20.9	0.07	0.17	0.002	ND	0.005	0.11	0.211	0.031	ND
Indonesia #1	19.4	0.16	ND	0.189	ND	0.020	0.69	1.43	0.052	ND
Indonesia #2	32.3	0.14	0.57	0.041	ND	0.008	0.38	0.667	0.147	ND
Indonesia #3	31.9	0.23	0.09	0.036	ND	0.010	0.30	0.869	0.098	ND
Middle East #1	32.5	0.14	ND	ND	ND	0.006	ND	0.074	0.024	ND
Middle East #1*	32.5	0.14	ND	ND	ND	0.007	ND	0.079	0.028	ND
Middle East #2	33.5	0.16	ND	ND	ND	0.016	ND	0.016	0.046	ND
North America #1	29.3	0.17	ND	0.003	ND	0.005	0.02	0.248	0.048	ND
North America #2	36.1	0.30	ND	0.018	ND	0.015	0.02	0.111	0.133	ND
North America #3	40.8	0.10	ND	ND	ND	0.007	0.02	0.033	0.050	1.56
North America #4	39.2	0.11	ND	0.368	ND	0.006	ND	0.022	0.079	ND
North America #5	22.6	0.13	ND	0.087	ND	0.006	1.13	0.864	0.173	ND
North America #5*	22.6	0.15	ND	0.090	ND	0.007	1.08	0.874	0.165	ND
North America #6	40.7	0.20	ND	0.011	ND	0.005	ND	ND	0.059	ND
North America #7	28.1	0.15	ND	0.036	ND	0.003	ND	0.167	0.046	ND
North America #8	13.3	0.28	0.19	0.206	ND	0.013	0.81	0.398	0.148	ND
North America #9	43.4	0.21	ND	ND	ND	0.003	ND	0.095	0.012	ND
North America #10	30.7	0.19	0.23	0.006	ND	0.011	ND	0.329	0.241	ND
North America #11	26.0	0.09	ND	0.014	ND	0.006	1.33	0.379	0.234	ND
North Sea	19.5	0.05	0.19	0.124	ND	0.005	0.67	0.069	0.055	ND
South America #1	12.0	0.08	ND	0.015	ND	0.010	0.27	0.117	0.068	ND
South America #2	19.2	0.14	ND	ND	ND	0.016	0.16	0.088	0.026	ND
South America #3	16.2	0.18	ND	0.095	ND	0.009	0.22	0.214	0.071	ND

Table 2 (Continued). Amount of metals in crude oils (data are in mg/kg oil).

	API Gravity	Mo	Ni	Pb	Sb	Se	Sn	Tl	V	Zn
Africa #1	35.0	0.49	3.20	0.008	ND	0.05	2.72	ND	0.13	4.06
Africa #2	37.1	0.50	0.33	0.010	0.001	0.03	0.11	ND	0.47	2.30
Africa #3	37.8	0.60	0.87	0.014	ND	N.D	0.81	ND	1.3	3.23
Africa #4	33.3	0.43	7.28	0.018	ND	0.02	1.50	ND	0.91	2.50
Asia	46.4	0.58	0.08	0.009	ND	0.04	9.66	ND	1.2	4.81
Central America	20.9	4.01	53.5	0.008	0.036	0.23	1.23	ND	320	0.58
Indonesia #1	19.4	0.85	24.1	0.025	0.010	0.04	3.26	ND	1.4	0.63
Indonesia #2	32.3	0.41	9.39	0.028	0.005	0.04	0.44	ND	1.2	6.04
Indonesia #3	31.9	0.41	4.62	0.015	0.010	0.03	1.30	ND	0.15	1.28
Middle East #1	32.5	0.47	4.32	0.009	0.008	0.08	0.90	ND	21	2.61
Middle East #1*	32.5	0.45	4.48	0.011	0.011	0.08	0.91	ND	21	2.61
Middle East #2	33.5	0.87	4.32	0.025	0.019	0.14	2.41	ND	7.2	4.21
North America #1	29.3	0.41	12.3	0.024	0.003	0.12	2.33	ND	33	2.30
North America #2	36.1	0.31	4.30	0.101	0.002	0.27	0.42	ND	20	3.70
North America #3	40.8	0.35	5.09	0.005	ND	0.06	0.31	ND	1.0	8.42
North America #4	39.2	0.48	2.28	0.045	0.005	0.04	2.43	0.004	4.6	3.96
North America #5	22.6	0.54	50.4	0.006	0.013	0.52	0.27	ND	45	3.54
North America #5*	22.6	0.53	51.8	0.005	0.012	0.52	0.27	ND	44	3.70
North America #6	40.7	0.62	0.30	0.035	0.012	0.05	0.54	0.004	0.44	2.04
North America #7	28.1	0.31	14.1	0.038	0.004	0.12	0.11	ND	40	2.89
North America #8	13.3	0.71	55.9	0.111	0.010	0.44	0.11	ND	100	0.59
North America #9	43.4	0.41	0.05	0.005	0.001	N.D	0.14	ND	0.36	ND
North America #10	30.7	0.53	9.97	0.069	0.009	0.13	0.49	0.002	0.66	10.9
North America #11	26.0	1.91	57.8	0.018	0.017	0.31	2.26	ND	120	3.39
North Sea	19.5	0.78	6.87	0.018	0.001	0.13	0.04	ND	42	1.10
South America #1	12.0	1.29	93.0	0.022	0.055	0.46	0.08	ND	370	ND
South America #2	19.2	0.71	36.4	0.020	0.028	0.24	0.18	ND	250	0.66
South America #3	16.2	0.97	50.3	0.149	0.022	0.43	1.45	ND	250	ND

ND = Not Detected

* = Duplicate Analysis

Table 3. Statistical summary of metals content of 26 crude oils (the data are in mg/kg oil).

	Ag	As	Ba	Be	Cd	Co	Cr	Cu	Hg
Mean	0.15	0.06	0.052	ND	0.010	0.27	0.270	0.081	0.06
Minimum	0.05	ND	ND	ND	0.003	ND	ND	0.012	ND
Maximum	0.30	0.57	0.368	ND	0.026	1.3	1.43	0.241	1.56
Detection Frequency (# per 26 Oils)	26	7	19	0	26	16	25	26	1
Method Detection Level	0.010	0.080	0.001	0.005	0.002	0.010	0.005	0.010	0.010
Suggested USEPA Reporting Limit	0.1	0.5	1	0.1	0.2	0.2	0.5	0.5	0.6

	Mo	Ni	Pb	Sb	Se	Sn	Tl	V	Zn
Mean	0.77	19.69	0.032	0.011	0.16	1.37	0.000	62.75	2.92
Minimum	0.30	0.05	0.005	ND	ND	0.04	ND	0.13	ND
Maximum	4.0	93.0	0.149	0.055	0.52	9.66	0.004	370.0	10.9
Detection Frequency (# per 26 Oils)	26	26	26	21	24	26	3	26	23
Method Detection Level	0.020	0.020	0.001	0.001	0.02	0.010	0.002	0.020	0.080
Suggested USEPA Reporting Limit	0.2	1	1	1	1	---	1	0.5	1

ND = Not Detected

The mean values for the oils were less than 1.5 mg/kg for all metals except nickel, vanadium, and zinc, which had mean values of 19.7, 62.8, and 2.9 mg/kg, respectively. Beryllium was not detected in any of the crude oils. Only one oil from the San Joaquin Valley in the State of California contained mercury at a concentration above the detection limit. Mercury in this oil has been previously reported, and its presence is believed to be due to the proximity of the oil reservoir to mercury (quicksilver) deposits [16]. Thallium was detected in only 3 of the oils, and arsenic was detected in only 7 of the 26 crude oils.

Evaluation of Human Health Risks From Metals in Crude Oils

One way of evaluating the potential health risk associated with metals in crude oils is to assume that crude oil has been spilled on soil and that people might come into direct contact with the impacted soil. The potential health risk can then be evaluated by comparing the concentrations of the metals in the impacted soil to the screening levels presented in Table 1.

The concentrations of each metal in crude oil, as presented in Table 2, were compared to the USEPA direct human contact PRGs and the TNRCC lowest residential PCLs shown in Table 1. This comparison indicates that for 23 of the 26 crude oils, the metals concentrations in the oils did not exceed any PCL or PRG for any metal. One of the crude oils contained arsenic at a concentration

greater than its PRG, and two contained vanadium at concentrations greater than its PCL. For the oil exceeding the arsenic PRG, the crude oil concentration in soil that would result in an arsenic concentration exceeding the PRG would be 666,666 mg/kg, or 66.7% total petroleum hydrocarbons (TPH). Similarly, for the oil containing the highest concentration of vanadium, the oil content in soil would have to be more than 78.4% TPH in order to exceed the vanadium PCL in Texas.

Therefore, it is highly unlikely that metals in soil from a single crude oil spill or a single application of oil to the land surface would result in a significant risk to human health. Sites that have received multiple applications of oil or oil-contaminated soils, such as a landfarm site, would require further study. Also, E&P wastes may contain higher concentrations of some metals than their parent crude oils due to corrosion processes, chemical additives, or metals in produced water, and more data may be required to evaluate their risks.

Evaluation of Ecological Risks From Metals in Crude Oils

The concentrations of metals in the 26 crude oils were compared to ecological SSLs to evaluate the potential need for performing ecological risk assessments at crude oil spill sites. As shown in Table 4, 12 metals do not exceed the lowest ecological SSL even at their maximum concentration in pure oil. Only chromium, mercury, molybdenum, nickel, tin, and vanadium are present at levels that would limit the amount of crude oil in soil. For all metals except vanadium, maximum crude oil concentrations of 60,000 mg/kg (6%) in soil would result in maximum metals concentrations below their respective ecological SSLs.

Table 4. Comparison of lowest ecological benchmarks with the maximum concentrations found in 26 crude oils.

Chemical	Lowest Ecological Benchmark¹ (mg/kg)	Maximum Concentration in Crude Oil (mg/kg oil)
Antimony	5	ORNL-P 0.055
Arsenic	10	ORNL-P 0.567
Barium	500	ORNL-P 0.368
Beryllium	4	CCME-A <0.005
Cadmium	3	CCME-A 0.026
Chromium	0.4	ORNL-E 1.43
Cobalt	20	ORNL-P 1.33
Copper	60	ORNL-E 0.241
Lead	50	ORNL-P 0.149
Mercury	0.1	ORNL-E 1.56
Molybdenum	2	ORNL-P 4.01
Nickel	30	ORNL-P 93
Selenium	1	ORNL-P 0.52
Silver	2	ORNL-P 0.296
Thallium	1	ORNL-P 0.004
		CCME-A
Tin	2	CCME-A 9.66
Vanadium	2	ORNL-P 370
Zinc	50	ORNL-P 10.9

- 1) Sources of lowest ecological benchmarks are: ORNL-P = screening benchmark to protect terrestrial plants [12]; CCME-A = CCME remediation criteria for agricultural land-use [13]; ORNL-E = screening benchmark to protect earthworms [11].

Vanadium is the limiting metal for many of the crude oils. For the crude oil containing the highest level of vanadium (370 mg/kg), the maximum concentration of crude oil in soil that would not exceed the lowest vanadium SSL is 5,400 mg/kg. A maximum concentration of 10,000 mg/kg (1%) crude oil in soil would be protective for all oils, except for those from Central and South America. For the North American crude oils analyzed (which contained as much as 120 mg/kg vanadium), 16,000 mg/kg or 1.6% crude oil would not exceed the lowest vanadium ecological SSL.

The lowest ecological SSL for vanadium is a benchmark derived by ORNL and it is based on effects in terrestrial plants. It is possible that this benchmark is overly conservative, since it is almost 30-times lower than the average background concentration for vanadium in soil in the United States. Therefore, it is unlikely that vanadium would pose a significant risk to ecological receptors even at concentrations exceeding 1% crude oil in soil.

Based on our comparison of metal concentrations in crude oils to ecological SSLs, it is clear that there is no need to routinely perform ecological risk assessments for metals at sites contaminated by crude oil spills and/or historic releases. It may be necessary to perform a screening risk assessment to determine if site-related metals could potentially be of ecological concern at those sites for which other ecological pathways and receptors are important (such as wildlife and aquatic organisms) or at sites that have received multiple applications of oil.

Conclusions

Twenty-six crude oils were analyzed for 18 metals. Evaluation of the human health risk associated with soil containing crude oil showed that the potential risk was not significant at total oil concentrations in soil well above current management levels of 10,000 mg/kg TPH, used in many states. The amount of metals in 10,000 mg/kg TPH would also be protective of soil invertebrates, plants, and soil microbial communities. Vanadium may be of ecological concern only in some heavy crude oils from Central and South America.

It is apparent that acceptable levels for crude oil in soil based on the potential human health effects of metals are well above those that would be expected to produce unacceptable aesthetic effects. Overall, the concentrations of these metals in crude oils are unlikely to be a major risk management consideration at crude oil spill sites. Therefore, routine analyses for metals in soils at crude oil spill sites is not recommended.

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Application of Risk-Based Decision-Making for International Exploration and Production Site Management

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Introduction

In general, the fundamental process of risk-based decision-making (RBDM) is understood and accepted in the United States. In fact, as discussed in previous chapters, several states have incorporated RBDM into their site remediation programs. However, for most countries outside of North America and Europe, the concept of RBDM is relatively new or unfamiliar. A few international agencies, such as the Canadian Council of Ministers of the Environment [1] and the Dutch Directorate-General for Environmental Protection, Department of Soil Protection [2] have recently proposed or adopted risk-based approaches to derive regulatory levels for total petroleum hydrocarbons (TPH). Appropriately, they have utilized the same health risk-based concepts as those used in the United States as they are equally applicable to sites anywhere in the world. Moreover, in developing specific action levels for its program, each agency has incorporated specific assumptions that reflect conditions in its own part of the world to ensure that they are protecting the health of their citizens.

However, in other areas of the world this is not the rule. Most regulatory programs appear to more commonly set cleanup criteria based on a review of levels that have been set by North American or European agencies, rather than on a site- or even country-specific basis. The assumptions that were used by the North American or European agencies in setting cleanup levels are rarely reviewed to determine whether they are indeed appropriate for the new application in a given country. It is incorrect to merely assume that United States or European calculations, which reflect potential exposures in those parts of the world, are necessarily appropriate for other parts of the world. In order to develop meaningful regulatory programs and cleanup levels, adequate consideration must be given to factors such as differences in lifestyles, climate, geology, etc., which apply to different parts of the world. This chapter presents two examples in which RBDM and risk-based screening levels (RBSLs) were applied to exploration and production (E&P) sites in Nigeria and Indonesia. These examples demonstrate some of the important factors that must be considered in applying RBDM at international locations.

Developing RBSLs for Nigerian Sites

In the following example, a generic conceptual site model for a crude oil terminal in a Nigerian delta is developed. The focus of this example is on human health considerations, not potential ecological impacts. This example is not a comprehensive, site-specific risk assessment; rather it is simply an example of how a RBDM program might be implemented at a Nigerian site [3]. Prior to applying RBDM at Nigerian sites, the Nigeria Department of Petroleum Resources and other stakeholders would need to be consulted regarding proper use of Nigeria-specific parameters and policy decisions.

Site Description

The generic site in this example is assumed to be a large crude oil terminal located adjacent to a major river delta. Spills occurring at the site are assumed to be contained within the site boundaries, and it is assumed that there are no floating hydrocarbons on the water table. The soil at the site is sandy fill and maximum depth to groundwater is 3 feet. However, shallow groundwater is brackish and thus non-potable. Drinking water for the site is supplied by water wells that draw from 1,800 to 2,000 feet below ground surface.

Employees live on the site in company housing constructed of concrete blocks. The buildings have windows and are air conditioned. Workers are on duty for 7 days, then have 7 days off when they leave the terminal. The site is adequately protected from trespassers by a fence and guards, so a trespasser risk scenario does not need to be considered. Workers at the terminal wear protective equipment including long pants and long-sleeved shirts, boots, and hard hats.

There is residential housing just outside the fenced terminal. This housing is also constructed of concrete blocks, but these are typically open-air buildings, (i.e., not air conditioned). Subsistence fishing in the nearby river is the main occupation. Residents may grow their own vegetables, but there is no large scale farming or grazing nearby.

A conceptual site model (CSM) is provided in Figure 1 illustrating the exposure pathways that may occur in case of a leak or spill of crude oil at the site. Workers may be exposed via direct contact with soil, incidental ingestion of soil, or inhalation of vapors or soil particles from surface soil. Exposure may also occur via inhalation of vapors from subsurface soil. It is unlikely that workers would be exposed to hydrocarbons via drinking groundwater because the shallow groundwater aquifer is not used as a potable water source, and it is unlikely that hydrocarbons would migrate more than 1,800 feet, the depth of the drinking water wells.

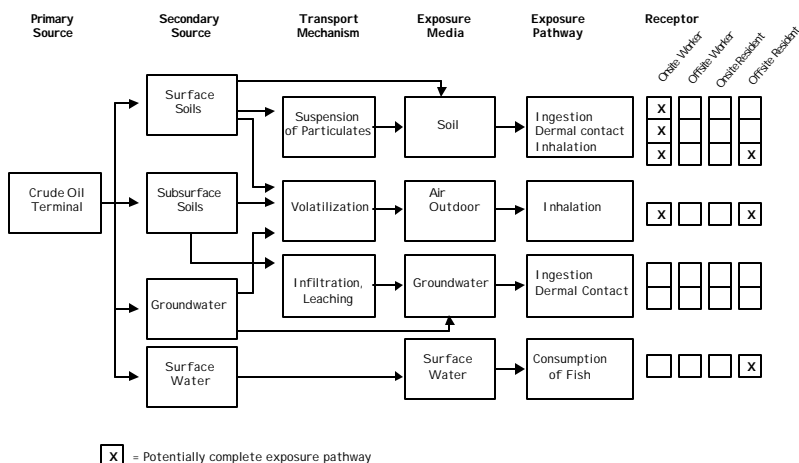


Figure 1. Potential exposure pathways at a generic oil terminal site in Nigeria.

The nearby residents use rainwater as a drinking water supply. Therefore, it is assumed that the local residents would only be exposed via inhalation of vapors from surface or subsurface soils and inhalation of surface soil particles, as long as the spill or leak was contained within the fenced terminal site. At this site, consideration should also be given to the potential impacts to surface water from hydrocarbon migration from the groundwater to the river. If hydrocarbons migrate to the river, there is a potential human health exposure pathway related to ingestion of fish caught in the river.

Exposure Parameters and Equations

The RBSL calculations followed the general approaches and algorithms used by the American Society for Testing and Materials (ASTM) [4], the Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG) [5], and the Petroleum Environmental Research Forum (PERF) [6]. The variables and the specific exposure assumptions used in the analysis are presented in Tables 1 and 2. These are also consistent with those presented by ASTM [4]. However, a few modifications were made to better reflect current risk assessment practices and to better address Nigeria-specific parameters.

Table 1. Receptor-specific parameter values used for the RBSL calculations.

Parameter	Units	Resident – Adult	Resident – Child	Worker
Lifetime	Years	52	52	52
Body Weight	kg	70	15	70
Exposure Duration	Years	24	6	25
Exposure Frequency	d/Year	365	365	183
Soil Ingestion Rate	mg/d	NA	NA	100
Inhalation Rate	m ³ /d	22	10	22
Soil to Skin Adherence Factor	mg/cm ²	NA	NA	0.2
Skin Surface Area Exposed to Soil	cm ²	NA	NA	7,000

NA = Not applicable, because inhalation of vapors and soil particles is the only exposure pathway.

Table 2. Media and source geometry parameter values used for the RBSL calculations.

Parameter	Units	Value
Lower Depth of Surficial Soil Zone	cm	100
Fraction Organic Carbon in Soil	g OC/g Soil	0.002
Particulate Emission Rate	g/cm ² -s	2.3E-12
Wind Speed Above Ground Surface in Outdoor Air Mixing Zone	cm/s	225
Width of Source Area in Major Direction of Wind	cm	1500
Outdoor Air Mixing Zone Height	cm	200
Volumetric Air Content in Vadose Zone Soils	(cm ³ Air)/(cm ³ Soil)	0.26
Total Soil Porosity	(cm ³ Voids)/(cm ³ Soil)	0.38
Volumetric Water Content in Vadose Zone Soils	(cm ³ H ₂ O)/(cm ³ Soil)	0.12
Soil Bulk Density	g/cm ³	1.7
Averaging Time for Vapor Flux	s	= Exposure Duration (see Table 1)

Two receptors were considered for the generic Nigerian crude oil terminal described above: an onsite worker and a resident adjacent to the site. The worker is assumed to be at the site half of the year (approximately 183 days). For many workers in the United States, the exposure time (used in the inhalation calculations) is assumed to equal 8 or 9 hours per day (hr/day). Because the onsite workers in this example are at the site 24 hr/day, the exposure time was adjusted to 24 hr/day. It is possible that the workers could come in direct contact with residually impacted soil, i.e., soil containing oil that has been left in place after emergency response cleanup has occurred. The RBSLs developed in this paper are for long-term worker exposures to oil impacted soil. The remediation worker who handles the spill initially, but only over a short period of time, is not addressed in this analysis.

The exposure pathways considered for the workers are incidental ingestion of soil, dermal contact with soil, and inhalation of soil vapor and particulate emissions. While on-duty, the workers wear full protective clothing and it is not likely that incidental ingestion and dermal contact would actually occur. These exposure pathways were included to take into consideration the times when workers may be off-duty and wearing lighter clothing, playing games like soccer, or doing other miscellaneous activities around the site. The parameter values assumed for the workers are shown in Table 1. The average lifespan in Nigeria was obtained from the international database of the United States Census Bureau [7]. The soil ingestion rate of 100 mg (per day) is twice the value normally used in the United States for industrial scenarios, but it seems appropriate given that the Nigerian workers are at the site for a much longer day than workers in the United States. The skin surface area of 7,000 cm² assumes that the worker typically wears shorts and a short-sleeved shirt when off-duty, but still on site [8]. The inhalation rate of 22 m³/day is recommended by the World Health Organization [9] and is similar to the value typically used in the United States. [8]. Worker exposure due to inhalation of indoor air is not included in this example because of the many site-specific parameters that must be investigated prior to calculating RBSLs for this pathway.

The resident is assumed to live at the site's property boundary. Because spills occurring at the site are assumed to be contained within the property boundary, the resident will not come in direct contact with the oil. Vapors and soil particulates covered with oil may be carried by the wind to the residences, and therefore the exposure pathways considered for the resident will be the inhalation of vapor and dust emissions. When calculating risk from non-carcinogenic chemicals, the degree of risk is calculated by comparing the estimated average daily dose with an acceptable dose (the reference dose, or RfD). For residential exposures to non-carcinogenic chemicals, it is standard risk assessment practice to assume that the receptor is a child. Children typically have high inhalation and ingestion rates relative to their body weight, and therefore they are usually the receptor with the greatest potential risk because they can experience the highest average daily dose. The exposure parameters used in this analysis are for a child 1 to 6 years in age, and they are shown in Table 1.

Nigeria Crude Oil RBSLs

Five crude oils from Nigeria were analyzed using the modified TPHCWG analytical method (see Chapter 4). Their American Petroleum Institute (API) gravities ranged from 24 to 38°. The calculated TPH RBSLs for non-carcinogenic effects are shown in Table 3 and they are in units of mg-TPH per kg-soil (mg/kg). For onsite workers, the RBSLs for surface soil exposure range from 38,000 to 45,000 mg/kg. These levels of crude oil will not result in

significant risk to adult workers who have direct contact with oil impacted soil. For offsite residents, the surface soil RBSLs range from 51,000 to 62,000. These levels of crude oil will not result in significant risk to children from inhalation of petroleum vapors or oily soil particles. (Note that if a spill were not contained within the terminal boundaries so that residents might be exposed to surface soils, the RBSLs could be lower by at least a factor of 10.)

For onsite workers and offsite residents the subsurface soil RBSLs are “RES.” The term “RES,” for residual saturation, is used to indicate that the oil does not pose a significant risk of adverse health effects even at residual levels in soil. (The RES concept applies only for the leaching to groundwater and volatile exposure pathways.)

Table 3. TPH RBSLs for Nigerian oils at a terminal site.

Oil Location/ Source	Surface Soil		Subsurface Soil	
	Offsite Resident Soil RBSL (mg/kg)	Onsite Worker Soil RBSL (mg/kg)	Offsite Resident Soil RBSL (mg/kg)	Onsite Worker Soil RBSL (mg/kg)
Crude Oil #1	51,000	38,000	RES	RES
Crude Oil #2	56,000	43,000	RES	RES
Crude Oil #3	60,000	45,000	RES	RES
Crude Oil #4	57,000	44,000	RES	RES
Crude Oil #5	62,000	41,000	RES	RES

RBSLs were not calculated for the potential fish ingestion pathway identified in the CSM. The only chemicals of potential concern in Nigerian crude oils that could be taken up by fish and transferred to people consuming the fish are the polyaromatic hydrocarbons. However, these chemicals are relatively insoluble in water and would not be expected to be dissolved in groundwater and transported to the river as a result of an onsite spill.

Developing RBSLs for Indonesian Sites

This section describes example TPH RBSLs developed for two different exposure conditions relevant to E&P operations in Sumatra, Indonesia: unrestricted land use and “indemnified” areas (non-residential). The TPH RBSLs correspond to TPH levels in soil that should pose no significant risk to human health with consideration given to oil composition, the current and future land use, populations likely to be exposed (children versus industrial workers), and exposure mitigation procedures.

There are two concerns to consider when setting cleanup levels or RBSLs in Sumatra – human health and ecosystem health.

The natural ecosystem in Sumatra has been disturbed in some areas due to logging, palm plantations, farming, and industrial activities. For these areas, it is most appropriate to consider the risk to human health along with current and future land use when setting cleanup levels or RBSLs. Therefore, RBSLs were derived for specific oil types and considering specific land use (e.g., unrestricted versus industrial or “indemnified” areas).

The science behind assessing risk to human health is well developed and has been described at length in this book. However, data on the impact of hydrocarbons in soil to specific ecological receptors (plants, animals, and insects) within an ecosystem are very limited, and the data that are available are largely from studies conducted with North American or European species. Therefore, it is impossible at this time to set acceptable TPH limits for protecting ecological receptors in undisturbed tropical rainforest ecosystems.

Site Description

Some oil production areas in Sumatra have been restricted to oilfield operations only and are termed “indemnified” or “restricted” use. These areas can therefore be evaluated much as industrial or commercial sites are evaluated in the United States. However, oil production may also co-exist with other land uses such as farming, residential areas, or plantations. These land uses were evaluated as “unrestricted” or similar to United States residential land use scenarios. Figure 2 illustrates a CSM for an unrestricted land use in Sumatra.

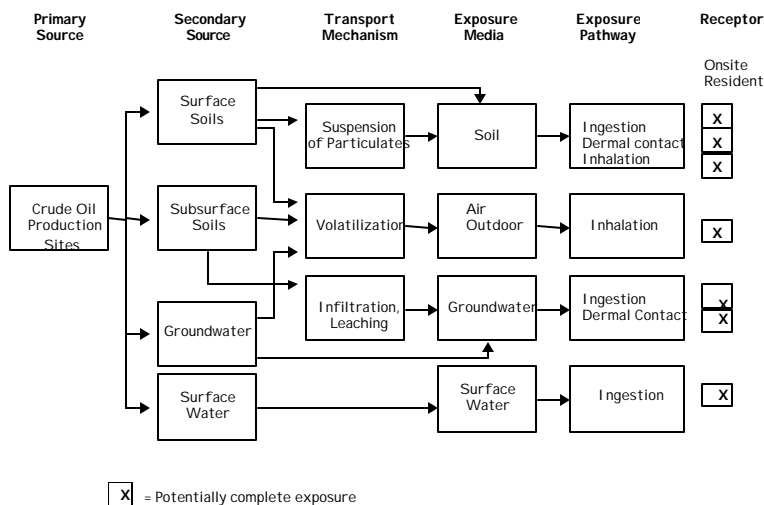


Figure 2. Potential exposure pathways at crude oil production sites in Sumatra, Indonesia for unrestricted land use.

Application of TPHCWG Method to Sumatran Crude Oils

Two main types of crude oils are produced in Sumatra: Sumatran Light (Minas crude oil is one example of this type oil), which has an API gravity of 32°, and Duri, which has an API gravity of 19.4°. These crude oils were analyzed by the modified TPHCWG analytical method and the results are shown below in Figure 3. Duri crude oil has a higher concentration of aromatic hydrocarbons and vacuum residuum (>C₄₄) than Minas crude oil, since the Duri oil has been biodegraded in the reservoir. Sumatran Light oils like Minas are waxy crude oils and have high levels of large molecular weight alkanes.

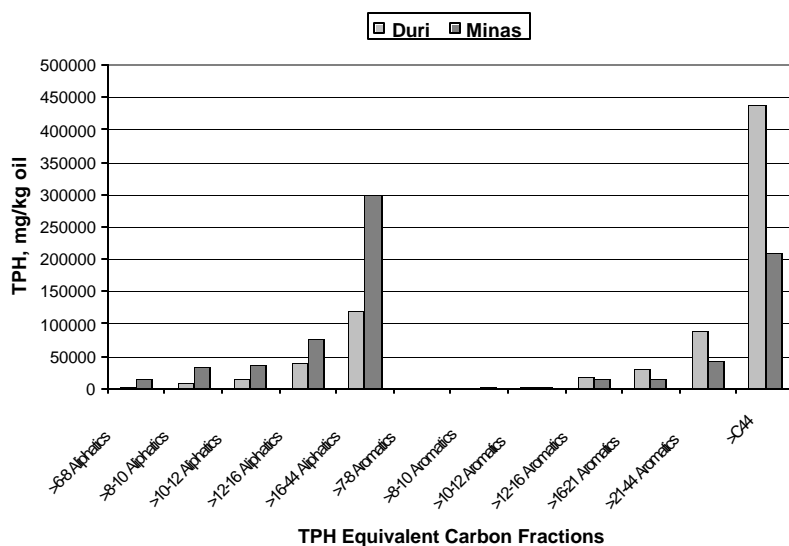


Figure 3. The TPH fractions [aliphatic and aromatic] and vacuum residuum >C₄₄ fraction for Minas and Duri oils.

RBSL Calculations for Crude Oils in Soil

The exposure assumptions commonly used in the United States were reviewed for their suitability for deriving TPH RBSLs to be used in Indonesia. Very little published information is available for developing Indonesia-specific exposure parameters. A few exposure parameters were modified based on World Health Organization information or site specific measurements (such as the fraction organic carbon in soil). These are described in Table 4.

Table 4. Indonesia-specific parameters used to calculate non-cancer TPH RBSLs.

Parameter	Abbrev.	Units	United States		Sumatra Indonesia		Rationale for Sumatra Value
			Residential (Child)	Comm./ Indust.	Residential (Child)	Comm./ Indust.	
Body Weight	BW	kg	15	70	12	60	Average body weight as described by World Health Organization for adult workers [9]. Body weight for child assumed to be proportional to difference between United States and Sumatra adult body weights [8].
Ingestion Rate: Soil	IRsoil	mg/Day	200	50	300	100	United States recommended soil ingestion rate for people involved in activities with heavy soil contact [8].
Inhalation Rate: Air-Outdoor	IRair-out	m ³ /Day	10	20	15	22	World Health Organization recommendation for commercial/industrial scenario [9].
Ingestion Rate: Water	IRw	L/Day	1	1	1.5	2	World Health Organization recommendation for adults in environments with high average temperatures [9]. Recommendation for child is 50% more than value assumed for United States child [8].
Skin Surface Area	SA	cm ² /Day	2,900	3,160	3,900	4,100	Skin surface area for Sumatra commercial/ industrial scenario corresponds to a person wearing shorts, shoes and a short-sleeved shirt [8]. Surface area for Sumatran child corresponds to a person wearing shorts and a sleeveless shirt [8].
Exposure Frequency	EF	Days/Year	350	250	365	365	Conservative assumption based on best professional judgment.
Fraction Organic Carbon in Soil	Foc	g/g	0.01	0.01	0.002	0.002	Measured value for total organic carbon content of Indonesian soils.

RBSLs for Restricted and Unrestricted Land Use

RBSLs were developed for oily soil using an unrestricted land use scenario. For this situation, RBSLs of 1,500 mg/kg TPH were calculated for Duri and 2,500 mg/kg TPH for Sumatra Light-type crude oils/wastes. Unrestricted use includes such high exposure activities as living (children and adults) on the site soil, constructing ponds, and using groundwater underneath the site as the sole water

supply. These RBSLs apply to TPH concentrations in surface soils, roads, oil spills, or oily pit sites that are located on or near places where people live.

The RBSLs for unrestricted land use are low due to the living conditions in a largely rural, developing region like Sumatra. The limiting pathways are dermal exposure, soil ingestion, and soil particle inhalation. Leaching to groundwater and volatile emissions will not usually be pathways of concern due to the low concentrations of benzene (<50 mg/kg oil) and other low molecular weight aromatic hydrocarbons in both Duri and Sumatra Light crude oils.

For restricted land use the RBSLs are much higher. The TPH RBSL for Duri crude oil is 18,000 mg/kg TPH and is 30,000 mg/kg TPH for Sumatra Light-type crude oils. This is due to lower amounts of exposure for industrial oil field workers.

Conclusions

The RBDM process is a scientifically defensible, flexible, yet standard process that can be used to develop international RBSLs. Simply adopting cleanup standards that have been developed by European or North American regulatory agencies for conditions in their countries will not provide meaningful standards for developing countries.

At a generic terminal site in Nigeria, a RBDM approach is used to determine potential receptors and complete exposure pathways. In the example presented, TPH RBSLs are needed for three commercial worker pathways and two residential exposure pathways. Similarly, example RBSLs were developed for use in Sumatra Indonesia based on two land use scenarios. For both countries, exposure parameters were modified to be protective of the way people live and may be exposed to chemicals in their environments. In cases where site conditions exceed these RBSLs, they can be used by a site manager as cleanup levels or a more detailed Tier 2 or 3 risk assessment could be performed. It may also be possible to reduce risk to human health by taking actions to eliminate some of the pathways of concern.

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The Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG) Analytical Method: *Characterization of C₆ to C₃₅ Petroleum Hydrocarbons in Environmental Samples*

- **Total Petroleum Hydrocarbons**
- **Aliphatic Hydrocarbons**
- **Aromatic Hydrocarbons**
- **Approximate Boiling Point/Carbon Number Distribution**

1.0 Scope and Applications

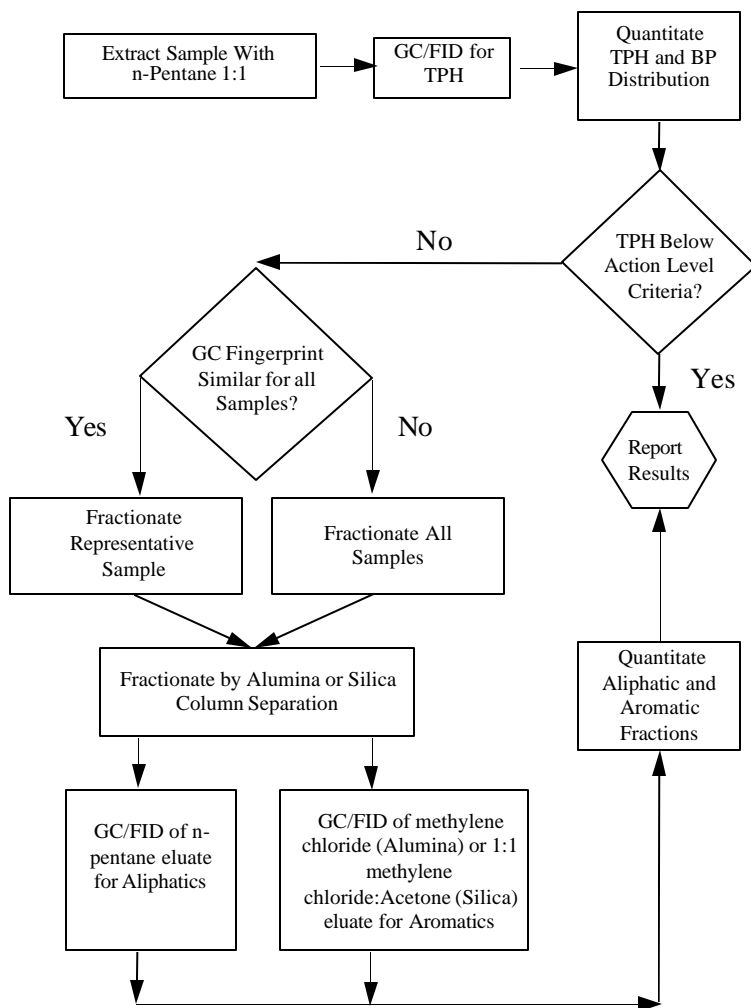
- 1.1 This gas chromatographic method is designed to determine the concentrations in soil and water of petroleum hydrocarbons from n-hexane (C₆) to n-pentatriacontane (C₃₅); an approximate boiling point range from 70°C to 500°C. This includes the gasoline, diesel range, and some portions of heavier fuels and lubricating oils. This method also describes the separation of the petroleum hydrocarbons into their aliphatic and aromatic fractions.
- 1.2 This method describes the characterization of the total petroleum hydrocarbons, the aliphatic, and the aromatic fractions into approximate carbon number/boiling ranges with respect to n-alkane markers. **See Figure 1 for overall method options and when to apply them.**
- 1.3 This method can be used to measure concentrations of individual target analytes. When target analyte information is desired, quantitation should be performed from the aliphatic or aromatic fractions rather than from the unfractionated extract. This will minimize the error due to coelution problems. However, target analytes are best determined using EPA Methods 8021, 8260, or 8270, where appropriate [1].
- 1.4 This method uses flame ionization (FID) as the mode of detection. The response of the FID is generally equal for all

hydrocarbons on a weight and effective carbon number basis [2].

- 1.5 The method reporting limit is estimated to be 50 mg/kg in soil and 5 mg/L in water depending on the number of hydrocarbon components present in the C₆ to C₃₅ range. A limited interlaboratory evaluation of the method for total petroleum hydrocarbons in soil and in water has been conducted in Texas to validate TNRCC TX Method 1005 [3]. In addition, a previous version of this method (using a split mode of injection) for total petroleum hydrocarbons in soil was subjected to an interlaboratory study conducted by The American Petroleum Institute [4]. It was found to have a PQL from 50 to 104 mg/kg (depending on the definition of PQL), an average accuracy of 84%, an average single analyst relative standard deviation (RSD) of 13%, and an average overall RSD of 30%. A similar study performed on this approach and the fractionation procedure by a single analyst showed an average accuracy of 80% with an average overall RSD of 6%. Also, an independent laboratory evaluation of this method resulted in a single analyst average accuracy of 111% and an overall RSD of 10%. Additional evaluation of this method has been done by the American Association of Railroads for applicability for diesel range materials [5] and by A.D. Little, Inc., for applicability to crude oil impacted soil. The latter effort studied the efficiency of n-pentane as an extraction solvent compared to methylene chloride and of vortex mixing versus Soxhlet. Both solvents and extraction mechanisms were found to be equivalent.
- 1.6 Petroleum and petroleum products with the majority of hydrocarbon components in the 70°C to 500°C boiling point range can be accurately extracted and measured by this method. This range includes gasoline, kerosene, Diesel/Fuel Oil No. 2, some lubricating oils, and portions of other heavier oils.
- 1.7 This method should be used by, or under the supervision of, analysts experienced in the use of solvent extraction, solid phase fractionation, and gas chromatography. The analysts should also be skilled in the interpretation of capillary gas chromatography data (specifically petroleum hydrocarbon pattern recognition), quantitation using computerized data acquisition, and use of peak processing software with baseline and peak grouping functions.

- 1.8 This method was originally developed to characterize petroleum hydrocarbons for proper remediation technology of impacted soils. Separation of the petroleum hydrocarbons into an aliphatic and an aromatic fraction was developed to provide data in the appropriate format to support the Total Petroleum Hydrocarbons Criteria Working Group (TPHCWG) risk-based corrective action approach to waste site remediation. This approach is based on the fate and transport and toxicological properties of petroleum hydrocarbon compound classes [6].
- 1.9 The extraction and fractionation procedure can take as little as 15 minutes to perform per sample. GC analyses may take 20 to less than 90 minutes depending on the chromatographic column used and the GC parameters. Three separate GC analyses per sample are required to obtain total petroleum hydrocarbons, total aliphatics, and total aromatic information. It is recommended that the sample extract be analyzed first to determine the type of petroleum hydrocarbons (if any) in the sample before proceeding with the fractionation step. Additionally, this information can be used for potential source identification, to assess if there are different types or distributions of petroleum hydrocarbons in a sample, or to determine if fractionation is necessary. If required, all or some of the sample extract may be fractionated into aliphatic and aromatic fractions, which are then analyzed by GC.

Figure 1: Overall Method Options for Characterization of Petroleum Hydrocarbons



2.0 Summary of Method

- 2.1 This method involves extraction of a soil or a water sample with n-pentane and analysis of a portion of the extract using gas chromatography with a flame ionization detector (GC-

FID). For additional characterization, fractionation of the petroleum hydrocarbon extract is accomplished by solid phase separation of another portion of the extract using alumina (similar to EPA Method 3611 [7]) and eluting with n-pentane to obtain an aliphatic fraction followed by elution with methylene chloride to obtain an aromatic fraction. Alternatively, fractionation may also be done using silica gel (similar to EPA Method 3630C [8]). Silica gel may be more suitable for samples with a wide boiling point distribution of hydrocarbons. Silica gel may also be better for the fractionation of the higher molecular weight polynuclear aromatics (PNAs). In the silica gel procedure, a 1:1 mixture of acetone:methylene chloride is used to elute the aromatic compounds. Other fractionation procedures, such as automated HPLC methods, may also be used. The fractions are also analyzed using GC-FID. The extract as well as the fractions can be further characterized by subdividing the chromatographic data into approximate boiling point/carbon number ranges with respect to n-alkane markers.

- 2.2 This method allows choices of standards for calibration. Either mixtures of single hydrocarbon components, petroleum products (such as gasoline or diesel), or mixtures of petroleum products can be used. It is strongly encouraged that petroleum products similar to those present as contaminants in the samples be used if possible.
- 2.3 This method is based in part on USEPA Methods 8000, 8015, and 8100, SW-846, "Test Methods for Evaluation of Solid Waste," 3rd Edition [1]. It is also similar to the Massachusetts Department of Environmental Protection Method for the Determination of Extractable Petroleum Hydrocarbons (EPH) [9]. This method is similar (for total petroleum hydrocarbons) to Washington State WTPH-HCID [10]. It was developed at Shell Development Company by I.A.L. Rhodes, L.P. Brzuzy, et al. [11-13]. This method was the basis for TNRCC TX Method 1005 [3].
- 2.4 This method uses n-pentane for the extraction of soil and water samples. Spiking studies done during method development and subsequent experiments at several laboratories with spiked and field samples show that n-pentane is equivalent to methylene chloride in extraction efficiency of hydrocarbons. The soil types ranged from sand to loam to clay. In addition, the vortexing extraction as well as Soxhlet

extractions were found to be equivalent (unpublished PERF project results with crude oil in soil samples). Recent published work by the University of Toronto indicates that n-pentane is an excellent solvent for extraction of hydrocarbons from water [14].

3.0 Definitions

- 3.1 **Total Petroleum Hydrocarbons (TPH)** are defined as all gas chromatographic peaks eluting after the solvent (n-pentane) starting with and including n-hexane (nC_6) to n-pentatriacontane (nC_{35}). This definition includes aliphatic and aromatic hydrocarbons. The petroleum hydrocarbons in a sample (if any) may not encompass the entire range. If the range of compounds present is narrower, then it is best to report on the observed range only. This information is useful for product or source identification. There may be non-hydrocarbon compounds that elute in this range (such as chlorinated solvents, ketones, alcohols, etc.). However, such compounds usually appear as discrete peaks and do not match typical petroleum product fingerprints. In some cases, such as when the samples contain crude or motor oil, only the portion within the nC_6 to nC_{35} will be measured as TPH.
- 3.2 **Aliphatic Hydrocarbons** are defined as those compounds detected from n-hexane (nC_6) to n-pentatriacontane (nC_{35}) (inclusive) in the chromatogram of the aliphatic fraction.
- 3.3 **Aromatic Hydrocarbons** are defined as those compounds detected from n-hexane (nC_6) to the retention time of n-pentatriacontane (nC_{35}) in the chromatogram of the aromatic fraction. The first aromatic compound is benzene.
- 3.4 **Approximate Boiling Point/Carbon Number Distribution** is defined as the subdivision of the chromatogram into sections that correspond to boiling point and/or volatility of n-alkanes. The gas chromatographic separation is achieved using a column that separates components based primarily on boiling point differences. This separation can be correlated to approximate carbon number. For example, $>C_7$ to $\leq C_8$ indicates those hydrocarbons that elute after n-heptane and up to and including n-octane. This range includes most, but not all, of the C_8 hydrocarbons. Branching lowers the boiling points of hydrocarbons relative to their n-alkane isomers. Cyclization, or ring structures, raises the boiling point higher

than the n-alkanes of the same carbon number. Thus, there are some C₈ hydrocarbons that elute before n-heptane and there are some that elute after n-octane, including the aromatics ethylbenzene and the xylenes.

This method allows for data reporting between each carbon range or for reporting within wider carbon ranges depending on data quality objectives. The TPHCWG has defined fractions based on different properties that affect the fate and transport and/or toxicity of petroleum hydrocarbon components.

- 3.5 **Aliphatic Hydrocarbon Standard** may be used to calibrate the analysis of the aliphatic or n-pentane fraction. The standard may be prepared from a mixture of n-alkanes and branched alkanes in n-pentane. This standard is not a requirement since it is recommended that a petroleum product or mixed products be used as standards for a single calibration that can be applied to extract and fractions.
- 3.6 **Aromatic Hydrocarbon Standard** may be used as an option to calibrate the analysis of the aromatic fraction. The standard can be prepared from a mixture of benzene, toluene, ethylbenzene, xylenes, C₃-benzenes (such as n-propylbenzene), C₄-benzenes (such as t-butylbenzene), and polynuclear aromatics (such as the EPA target PNAs) prepared in methylene chloride. As indicated in 3.5, this standard is not required.
- 3.7 **Locator Mix Standard** will be used to determine the ranges C₆ to C₃₅ and the individual ranges specified in Table 2.
- 3.8 **An Analytical Batch** is defined as a set of 1 to 20 samples prepared on the same day.

4.0 Interferences

- 4.1 Other organic compounds, including vegetable and/or animal oils and greases, organic acids, chlorinated hydrocarbons, phenols, and phthalate esters are measurable under the conditions of this method. However, if present, the characteristic petroleum hydrocarbon patterns will be altered. These compounds will be quantified as part of the TPH, but the data should be flagged as presumptively containing a significant amount of such compounds. The aliphatic and

aromatic fractions may have less susceptibility to interferences from some types of materials because the fractionation process may remove the interference.

- 4.2 Sample contamination due to sample preparation may be minimized by the use of disposable glassware. A reagent blank should be analyzed with each set of 10 or less samples to demonstrate that the system is free from contamination. If samples are expected to have high concentrations, it is also advised that solvent blanks be analyzed between GC runs to minimize contamination due to carryover.
- 4.3 High purity reagent grade or pesticide grade n-pentane, methylene chloride and acetone should be used to minimize contamination problems.
- 4.4 This method depends on correctly integrating a mass of unresolved peaks using a forced baseline. The resulting baseline, if drawn incorrectly, will have a significant effect on the concentration reported. It is imperative that chromatograms be checked (using a realistic scale relative to the chromatogram) for correct baseline extension. Blanks and/or a low level standard should be run to monitor for baseline drift every 10 samples.

5.0 Health and Safety Issues

- 5.1 The toxicity of the reagents used in this method has not been precisely defined. However, each chemical compound should be treated as a potential health hazard. Exposure to these chemicals should be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of Occupational Safety and Health Administration (OSHA) regulations regarding the safe handling of the chemicals specified in this method. A reference file or Material Safety Data Sheets (MSDS) should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety should be available and should be identified for use by the analyst.

6.0 Apparatus

- 6.1 Glassware
 - 6.1.1 All specifications are suggestions only.
 - 6.1.2 4 oz. (120 mL) amber glass wide-mouth jars.
 - 6.1.3 Vials
 - 6.1.3.1 10 to 40 mL glass vials with Teflon-lined screw caps.
 - 6.1.3.2 2 mL GC autosampler vials with Teflon-lined crimp caps.
 - 6.1.4 Disposable Pipettes: Pasteur.
 - 6.1.5 1 cm I.D. by 10 to 20 cm glass column with glass or Teflon stopcock.
 - 6.1.6 Volumetric flasks and graduated cylinders.
- 6.2 Microsyringes: 10 μ L to 1000 μ L.
- 6.3 Analytical balance capable of accurately weighing 0.0001 g should be used for preparation of standards. A top-loading balance capable of weighing to the nearest 0.01 g should be used for obtaining sample weights.
- 6.4 Vortex mixer.
- 6.5 Wrist action or horizontal shakers may be used for extraction.
- 6.6 Drying oven.
- 6.7 Gas Chromatography
 - 6.7.1 Gas Chromatograph: Analytical system which includes a splitless injector, column supplies, gases, and syringes. Electronic Pressure Control (EPC) is strongly recommended. A data system capable of storing and reintegrating chromatographic data and determining peak areas using a forced baseline and baseline projection is required. A gas chromatograph

capable of performing baseline compensation is desirable.

6.7.2 Recommended Columns

6.7.2.1 25/30 m x 0.25 to 0.53 mm ID fused silica capillary column with 0.25 to 1.5 μm film thickness (methyl silicone) or equivalent. Low bleed columns are preferred. Examples include MS-007 (Quadrex), DB-1 (J&W), and RTX-1 (Restek). DB-5 (J&W) may be used.

6.7.2.2 Other columns may be used if the elution of the compounds is based on boiling point. Capillary columns are recommended. See Section 9.3.2 for GC performance criteria.

6.7.3 Detector: A flame ionization detector (FID) is required.

6.7.4 Autosampler: An autosampler capable of making 1-4 μL sample injections is recommended.

7.0 Reagents and Standards

7.1 n-Pentane, methylene chloride, acetone. Reagent grade, pesticide grade or equivalent.

7.2 Sodium Sulfate (ACS): Granular, anhydrous. Purify by heating at 100°C for 4 hours in a shallow tray.

7.3 Alumina, basic or neutral, Brockman activity 1, 150 mesh. Activate by heating at 350°C at least 12 hours before using. Store at 110°C until ready to use. Alternatively, silica gel, 75-250 mesh. Activate at 110-130°C until ready to use. In addition, solid phase extraction cartridges, or automated HPLC methods may be used but equivalency must be demonstrated.

7.4 Calibration & Stock Standard Solutions: This method allows for the choice of calibration standard for quantitation. The use of either a petroleum product(s) standard or a standard composed of selected hydrocarbons is acceptable. The

selected hydrocarbon standard is required for the definition of carbon # retention windows and as a fractionation check solution. Unless noted, standards are prepared in the n-pentane listed in 7.1 above. Standard preparation should follow the guidelines outlined in EPA SW-846 Method 8000B.

7.4.1 Petroleum Product Calibration Standard for Total Petroleum Hydrocarbons, Aliphatic and Aromatic Fractions: The petroleum hydrocarbon calibration standard can be prepared by accurately weighing approximately 0.05 to 0.1 g (recorded to the nearest 0.0001 g) of a mixture of gasoline and Diesel #2 in a 1:1 (either by volume or weight) ratio and diluting to volume with n-pentane in a 10 mL volumetric flask. If only the gasoline range *or* the diesel range TPH is of interest, then the calibration standards should be prepared with either 0.100 g gasoline *or* 0.100 g diesel. This 1% standard should be kept refrigerated. Typical working concentration ranges are between 5 to 5000 µg/mL. Calibration standards may be prepared from a blend of selected hydrocarbons (as in Section 7.4.2).

7.4.2 Petroleum Hydrocarbon Calibration Standard, Approximate Boiling Point /Carbon Number Distribution Marker, and Fractionation Check Stock Standard: This standard can be used for several purposes: for TPH calibration, for retention time window/approximate boiling point distribution marker (locator mix standard), and for alumina/silica gel fractionation performance check. The stock standard can be prepared by accurately weighing approximately 0.01 g (recorded to the nearest 0.0001 g) of each of n-alkanes [n-hexane (C₆) through n-eicosane (C₂₀) as well as n-pentacosane (C₂₅), n-octacosane (C₂₈), and n-pentatriacontane (C₃₅)] and diluting to volume with n-pentane in a 50 mL volumetric flask. It is also suggested that this standard contain 0.01 g each of benzene, toluene, ethylbenzene, o,m,p-xylene, cumene, as well as some or all of the target PNAs (naphthalene, anthracene, pyrene, etc.). Table 1 lists the boiling points of the n-alkanes. The laboratory should determine the retention times. The approximate concentration of

this stock solution is 200 µg/mL per component. If this solution is to be used as a marker for retention time window/approximate boiling point distribution, accurate concentrations are not necessary. If the application requires that wider carbon ranges be used (ex: C₆ to C₁₀), this standard can be prepared with fewer n-alkane markers. This stock solution can be used for the determination of total petroleum hydrocarbons as well as the aliphatic and aromatic fractions if a component standard is preferred over a mixed product standard as described in 7.4.1 (please note limitations of this approach listed in 9.5.1). If available, a standard mix can be obtained from commercial suppliers.

- 7.4.3 Petroleum Products Reference Standards: To assist in the qualitative determination of product type or “fingerprint” of a possible petroleum product(s), it is recommended that a library of chromatograms be generated of gasoline, kerosene, diesel, motor oil, crude oils, and any other pertinent product for comparison purposes. A recommended concentration range is 1000 to 5000 ppm. These may be obtained from several chromatography supply vendors.

8.0 Sample Collection, Preservation, Containers, and Holding Times

- 8.1 Soil samples are collected in wide-mouth glass jars with Teflon-lined caps. Soils samples can also be collected and transported in core sampling devices [15]. Samples are stored at 4°C from the time of collection until extraction. Soil sample extraction and analysis should be performed within 14 days of collection. Depending on the analytes of interest and data quality objectives, other holding times may be applicable.
- 8.2 Water samples are to be collected by filling a 40 mL (volatile organics analysis) VOA vial with the sample and capping the vial with a Teflon septum cap (headspace free). Water samples may be preserved with HCl to a pH <2. Water sample analysis must be performed within 7 days of collection.

Table 1. Boiling points of n-alkanes used for the determination of approximate boiling point/carbon number distribution. Retention times based on GC conditions described in this method must be determined experimentally.

n-Alkane Marker	~ Boiling Point, ° C	n-Alkane Marker	~ Boiling Point, ° C
n-C ₆	69	n-C ₂₁	357
n-C ₇	98	n-C ₂₂	369
n-C ₈	126	n-C ₂₃	380
n-C ₉	151	n-C ₂₄	391
n-C ₁₀	174	n-C ₂₅	402
n-C ₁₁	196	n-C ₂₆	412
n-C ₁₂	216	n-C ₂₇	422
n-C ₁₃	236	n-C ₂₈	431
n-C ₁₄	253	n-C ₂₉	441
n-C ₁₅	270	n-C ₃₀	450
n-C ₁₆	287	n-C ₃₁	458
n-C ₁₇	302	n-C ₃₂	467
n-C ₁₈	316	n-C ₃₃	474
n-C ₁₉	329	n-C ₃₄	481
n-C ₂₀	343	n-C ₃₅	499

9.0 Procedures

9.1 Sample Extraction

9.1.1 Soil Extraction: Extract soil samples using a vortex mixer or shaker technique.

9.1.1.1 Weigh 10 g of sample in a 40 mL vial with Teflon cap. Record the weight to the nearest 0.01 g. If needed, add enough sodium sulfate to make a loose friable mixture (the use of sodium sulfate may not be necessary for dry soils). The sample should be free flowing prior to addition of the n-pentane. It is preferred that mixing of sodium sulfate with the sample be done as quickly as possible to minimize potential losses of volatiles. Add 10 mL of n-pentane, cap the vial, and proceed with the extraction.

- 9.1.1.2 For a method blank, weigh 10 grams of Ottawa sand or other blank standard soil and extract as a sample.
- 9.1.1.3 For laboratory control samples (LCS) weigh 10 grams of Ottawa sand or other blank standard soil. For matrix spikes, weigh a separate 10-gram portion of sample. Add 0.25 mL to 1.0 mL of stock solution to both the LCS and matrix spike as described in Section 7.4.1 and extract them like the samples.
- 9.1.1.4 Extract blanks, samples, LCS, matrix spike, and matrix spike duplicates by vortexing for at least 1 minute or shaking on a wrist action or horizontal shaker for at least 1 hour.
- 9.1.1.5 If particulate is suspended in the solvent layer or an emulsion forms, centrifugation may be necessary to obtain a clear solvent layer. Transfer a portion of the extract to autosampler vials for direct analysis of the extract for total petroleum hydrocarbons. The extract may be stored in vials with Teflon caps. Extracts should be stored at -15°C.
- 9.1.1.6 Anhydrous sodium sulfate may be used to aid in the drying and extraction of wet sediment or sludge samples. Weigh the sample into the vial then add up to 10 g of anhydrous sodium sulfate, cap and mix by vortexing. Add 10 mL of n-pentane, cap the vial, and proceed with the extraction.
- 9.1.1.7 If a sample of neat petroleum product, crude oil, or waste is to be analyzed, the sample should be diluted in n-pentane (1:50 to 1:100) and analyzed directly. Alternatively, approximately 0.01 g (~1 drop) of the material can be placed directly on the column for fractionation (Section 9.2).

9.1.2 Water Extraction: Extract water samples using a vortex mixer.

9.1.2.1 Remove sample in a 40 mL VOA vial from refrigeration and allow to come to ambient temperature. Remove approximately 10 mL of sample through the septum with a syringe. It is recommended that a needle be inserted into the septum at the same time to allow for flow of air into the vial as the 10 mL of water are removed. Dry the outside of the vial with a paper towel. Weigh the vial and its contents on a top loading balance and record the weight to the nearest 0.01 g.

9.1.2.2 Using a 5-mL glass syringe, add 3 mL of n-pentane through the septum of the 40 mL VOA vial.

9.1.2.3 For laboratory method blanks, perform the procedure as in Section 9.1.2.1 using a VOA vial filled with approximately 30 mL of reagent water.

9.1.2.4 For matrix spikes and laboratory control samples (LCS), perform the procedure as in Section 9.1.2.1, but add 0.1 mL of stock from Section 7.4.1 to 30 mL of a sample or distilled water prior to extraction.

9.1.2.5 Extract samples, LCS, blanks, matrix spikes, and matrix spike duplicates by vortexing for at least 1 minute.

9.1.2.6 Remove extract by pipette and store in Teflon capped vials at 4°C.

9.1.2.7 Discard the water from the VOA vial and dry the vial, lid, and septum in a drying oven at 70°C.

9.1.2.8 Reassemble the vial and weigh it on a top loading balance and record the weight to the nearest 0.01 g.

9.1.2.9 Determine the sample volume by subtracting the initial vial weight obtained in 9.1.2.1 from the dry vial weight obtained in 9.1.2.8.

9.2. Extract Fractionation: Fractionate extract into aliphatic and aromatic components, if required, to obtain information in format suitable for the risk based correction approach proposed by the TPHCWG [6].

9.2.1 Prepare the column by placing approximately 1 cm of moderately packed glass wool at the bottom of the column. Assemble the stopcock making sure that it turns smoothly.

9.2.2 Fill the column with about 10 mL of methylene chloride. Add approximately 4 grams of activated alumina to the column or if silica gel is used, 2 grams of activated silica gel). Ensure that it is packed uniformly by gently tapping the side of the column. Top the column with approximately 0.5 cm of sodium sulfate. Then rinse the column with at least 10 additional mL of methylene chloride. Let the solvent flow through the column until the head of the liquid in the column is just above the top of the column (alumina packing nearly exposed). Discard the eluted methylene chloride. Add about 2 mL of n-pentane. Open the stopcock and let the solvent flow until the liquid in the column is just above the top of the column. Add 10-20 mL of n-pentane in the same manner just described. Open the stopcock and let the n-pentane flow until the head of the liquid is just above the top of the column. Discard the eluant. The column is ready for use.

NOTE: The performance of the alumina or the silica gel is dependent on the particular lot number of alumina or silica gel from the manufacturer, the humidity of the laboratory environment, and the activation temperature. Each laboratory may need to raise or lower the activation temperature depending on their particular conditions to achieve optimal separation.

- 9.2.3 Add 1 mL of the sample extract to the column. Open the stopcock and start collecting the eluant immediately in a 10-mL graduated cylinder, a 10-mL volumetric flask, or any appropriate measuring vial. When the head of the n-pentane extract nearly reaches the top of the alumina or silica gel column, add n-pentane to the column in 1-2 mL increments while continuing to collect the eluant. It is best to add the solvent nearly dropwise with a pipette or wash bottle. Continue this approach until an accurately measured volume (8-10 mL) of the eluant is collected. Cap the vial and label this fraction "aliphatics."
- 9.2.4 Once the 8-10 mL of the n-pentane (aliphatic) fraction has been collected, proceed to collect in another graduated cylinder, volumetric flask, or appropriate measuring vial the aromatic fraction by elution with methylene chloride. This is done in the same manner as in 9.2.3 by collection of the eluant immediately after addition of methylene chloride in 1-2 mL increments or dropwise. It is critical that the first 3-4 mL be added carefully and slowly. Once 8-10 mL have been collected, cap the vial and label this fraction "aromatics." If silica gel is used, elute this fraction with a 1:1 mixture of acetone:methylene chloride.
- 9.2.5 Fractionation of neat petroleum products, crude oil, and wastes is done by directly placing on the alumina or silica gel column 1 drop of the sample or by weighing approximately 0.01 g of the sample, adding 1 mL of n-pentane and then proceeding with the fractionation as defined in Section 9.2.3.

NOTE: It is critical that extreme care be taken on the elution of aliphatic and aromatic fractions to optimize the fractionation process. This optimization can be achieved by allowing the extract to elute from the column as much as possible before the addition of additional solvent: run the sample nearly out of the column before more solvent is added. Add additional solvent in

small increments to the column to separate and obtain the fractions in narrow bands.

The amount of pentane and methylene chloride or acetone:methylene chloride used to elute the aliphatic and aromatic fractions, respectively, can be optimized experimentally. Use enough pentane to elute all the saturates. This may require as little as 8 mL, but no more than 12 mL of pentane. Recoveries of aliphatics should be greater than 80%. If more than 12 mL of pentane is used, elution of aromatic compounds in the aliphatic fraction may result. For the aromatic fraction, use enough methylene chloride to ensure that all the aromatic compounds, especially the PNAs, have eluted from the column. Again, recoveries should be greater than 80%. Minimizing the amount of solvent used will increase the sensitivity of the analysis by avoiding overdilution of the sample.

9.2.6 Extract concentrations exceeding 10,000 µg/mL TPH may need to be diluted to avoid alumina column overloading. Silica gel capacity has not been determined; it is recommended that extraction concentrations not exceed 10,000 µg/mL.

9.2.7 The blank, LCS, matrix spike, and matrix spike duplicate must also be fractionated with the sample batch.

9.3 Gas Chromatography

9.3.1 Gas Chromatographic Conditions

9.3.1.1 Oven Program: Set the initial column oven temperature to 10°C and hold for 1 to 5 minutes. Then ramp at 4 to 10°C/minute to 320°C and hold for 10 to 15 minutes. Alternatively, set initial column oven temperature to 30°C and hold for 3 to 4 minutes. Ramp at 10 to 20°C/minute to 300 to 320°C, hold for up to 10 minutes. Any oven program used must demonstrate adequate separation between the solvent and

n-hexane (the first compound to be included in the TPH measurement).

- 9.3.1.2 Sample/Autosampler Injection: 1 to 4 μ L splitless injection.
- 9.3.1.3 Carrier Gas: Helium at 15 psig for a 0.25 mm ID column or as recommended by column manufacturer (lower pressures are required for larger IDs). If electronic pressure control (EPC) is used, the pressure will be variable.
- 9.3.1.4 Make-up Gas: Nitrogen preferred (helium can be used (30 mL/min.).
- 9.3.1.5 FID hydrogen and air set to manufacturers' specifications.
- 9.3.1.6 FID Temperature: 325°C to 350°C.
- 9.3.1.7 Injection Port Temperature: 300°C to 325°C.
- 9.3.1.8 GC operated in splitless mode. Turn split on 1 minute after injection. Alternatively, a direct injection (Uniliner) technique may be used.

- 9.3.2 Performance Criteria: GC run conditions and columns should be chosen to produce chromatograms with adequate separation between the solvent front and n-hexane (the earliest eluting compound of interest that defines the beginning of the first carbon range). In addition, clear baseline resolution in the C₆ to C₁₂ range should be achieved.

NOTE: Adequate separation of n-hexane from the solvent front (n-pentane) may be difficult with thin film columns (<0.32 mm film thickness). The thin film columns facilitate the elution of hydrocarbons up to n-C₃₅ within a reasonable time. Thus, there may be some columns that may compromise the ability to analyze the entire C₆ to

C₃₅ range adequately. The thicker film columns work quite well in the C₆ to C₂₈ range.

9.4 Retention Time Windows

- 9.4.1 Before establishing windows for integration using n-alkanes as markers, make sure that the GC system is within optimum operating conditions. Make three injections of the boiling point distribution standard defined in 7.4.2 throughout the course of a 72-hour period.
- 9.4.2 Calculate the standard deviation of the absolute retention times for each individual component in the boiling point distribution standard.
- 9.4.3 The width of the retention time window for each analyte is defined as plus or minus three standard deviations of the mean absolute retention time established during the 72-hour period. If a standard deviation of 0.00 is obtained, check reference SW-846 8000B Section 7.6.3 for further instructions [1]. Analyst experience should be part of the interpretation of the chromatograms.
- 9.4.4 Alternatively, a default window may be chosen. This approach is preferred over the one described above because capillary columns are reliable with sufficient overall long-term stability to maintain retention time (RT) appropriately. This approach is also extremely simple. A window of ± 0.1 minutes should be adequate.
- 9.4.5 The laboratory should reassess retention time windows for each standard on each GC column and whenever a new GC column is installed.
- 9.4.6 TPH RT ranges are defined as beginning 0.1 minute before the RT of the beginning marker compound (n-hexane) and ending 0.1 minute after the RT of the ending marker compound (n-pentatriacontane or the last peak that elutes for a given sample if the last peak elutes earlier than n-pentatriacontane). This RT range is applicable for the determination of TPH, aliphatic TPH, and aromatic TPH.

- 9.4.7 The approximate boiling point/carbon number distribution for the samples can be determined using n-alkane to define carbon # ranges of interest. The chromatograms obtained from analysis of TPH, aliphatic TPH, and aromatic TPH can be subdivided into individual boiling ranges/approximate carbon numbers based on these RT windows. The TPHCWG has defined several aliphatic and aromatic fractions for the RBCA approach. These fractions encompass several carbon ranges which can be obtained the same way but using either addition of the individual carbon ranges or by defining wider carbon ranges for measurements. The marker compounds are defined in Table 1.
- 9.4.8 TPHCWG Aliphatic and Aromatic Fractions: The TPHCWG has defined approximate carbon ranges of aliphatic and aromatic fractions based on fate and transport considerations. The fractions are listed in Table 2. This method can provide this information by either defining the RT ranges using the corresponding n-alkane markers for the characterization of the aliphatic and aromatic fractions with the exception of the aromatic fraction where practical quantitation stops at C₃₅.
- 9.5 Calibration: Calibrate the GC system using the external standard procedure
- 9.5.1 The method takes advantage of the fact that the response of the FID is essentially the same for all hydrocarbons (on a weight basis) and based primarily on effective carbon number [2]. Any other compound containing heteroatoms will have some reduced response with respect to hydrocarbons because of lower carbon to hydrogen ratio. It is therefore not essential that calibration be performed using material similar to the material in the samples. For example, any gasoline, diesel, synthetic mixture, or single hydrocarbon can be used for calibration. However, because products such as gasoline or diesel are composed of more than 300 individual components, at low concentration of total product, many of the individual components are simply too

small to be detected and cannot contribute to the total signal detected and thus linearity falls off. Conversely, when synthetic standards are used, typically no more than 10-20 components are used and thus the TPH is distributed among a few peaks that can be all detected for all concentrations of the standards above the stated practical quantitation limits. The use of synthetic standards can result in underestimation of the TPH present in the samples.

Table 2. TPHCWG fate and transport fractions.

Aliphatics	Aromatics
$\geq C_6$ to C_8	$>C_6$ to C_7 (Benzene)
$>C_8$ to C_{10}	$>C_7$ to C_8 (Toluene)
$>C_{10}$ to C_{12}	$>C_8$ to C_{10}
$>C_{12}$ to C_{16}	$>C_{10}$ to C_{12}
$>C_{16}$ to C_{21}	$>C_{12}$ to C_{16}
	$>C_{16}$ to C_{21}
	$>C_{21}$ to C_{35}

9.5.2 External Standard Calibration Procedure: Guidance is provided for calibration and calculations using calibration factors. However, it is strongly recommended that a chromatographic data system be used for data acquisition and processing. The baseline may rise as a result of column bleed at the higher temperatures towards the end of the run. Baseline compensation may help in integration of the chromatogram over the background from column bleed.

9.5.2.1 Prepare calibration standards from one of the stock solutions described in 7.4.1 or 7.4.2 at a minimum of five concentration levels by adding volumes of the pertinent stock standard solutions to volumetric flasks and diluting to volume with n-pentane or methylene chloride. The following calibration levels are recommended: 20, 50, 100, 200, 500, 1000 $\mu\text{g/mL}$. Calculate the total concentration of the 7.4.2 multicomponent stock standard for TPH

calibration by adding all of the concentrations of the individual compound (ex: 200 µg/mL per component, if 20 components, then TPH is 4,000 µg/mL) before diluting to prepare the calibration standards.

- 9.5.2.2 Inject each calibration standard using the same injection volume (1 to 4 µL injections) and technique that will be used to introduce the actual samples into the gas chromatogram. Tabulate peak area responses against the concentration injected using a force baseline projection. The results can be used to prepare a calibration curve for quantitation. Linear and quadratic calibration fits may be adequate for the calculation of sample results. Alternatively, the ratio of the response to the amount injected, defined as the calibration factor (CF), can be calculated for the standard at each concentration. If the percent relative standard deviation (% RSD) is less than or equal to 25% over the working range, the average response factor can be used in place of a calibration curve. If linear regression analysis is used for quantitation, the correlation coefficient (R) must be at least 0.995.

$$\text{Calibration Factor (CF)} = \frac{\text{Total Area of Calibration Standard}}{\text{Concentration of Calibration Standard (}\mu\text{g/mL)}}$$

Note: It is recommended that area response from calibration standards be acquired in the same manner as samples.

$$\% \text{ RSD} = \frac{\text{Standard Deviation of 5 CFs}}{\text{Mean of 5 CFs}} \times 100$$

- 9.5.2.3 The calibration factor obtained in Section 9.5.2.2 can be used to calculate TPH, aliphatic hydrocarbons, and aromatic hydrocarbons. The same calibration factor

can be used to calculate the concentration of hydrocarbons present within the n-alkane markers used for defining the approximate boiling point/carbon number distribution. Alternatively, the boiling point distribution can be obtained from normalization of the entire chromatogram (nC₆ to nC₃₅) and determination of area percent within n-alkane markers. It is best to use a chromatographic data system to handle these calculations. A separate calibration file with the additional retention times should be established for the hydrocarbon ranges of interest to determine the approximate boiling point distribution and/or selected hydrocarbon ranges, both total and fractionated.

- 9.5.2.4 The working calibration factor or calibration curve should be verified on each working day by the injection of a mid-point calibration standard. If the concentration or response for these standards varies from the standard value or predicted response by more than $\pm 25\%$, a new calibration curve should be prepared. It is advisable to check instrument performance and reanalyze a low concentration standard as well to verify instrument performance and linearity.

$$\text{Relative Percent Difference} = \frac{R1 - R2}{R_{\text{avg}}} \times 100$$

where:

R1 = Standard value or average CF

R2 = Calculated value or CF

R_{avg} = (R1 + R2)/2

- 9.5.2.5 Calibration of Selected Target Analytes: Selected components (target compounds such as benzene, toluene, ethylbenzene, xylenes, PNAs, n-alkanes) can be measured individually if desired. Assuming an

equivalent calibration factor, the calibration curve or calibration factor developed above can be used for target analytes. Coelutions of these target compounds in complex hydrocarbon mixtures can be expected. This is more significant for the PNAs because of the large number of isomers that are present as the carbon number increases. The results from these analyses can result in overestimation of these target compounds. If necessary, confirmation and more accurate quantitation may be obtained by using EPA Methods 8021, 8260, 8270 [1].

9.5.2.6 Chromatographic Data System: The concentration of specific analytes or hydrocarbon ranges may also be calculated from a calibration curve by use of regression analysis.

9.6 Product Type Identification

9.6.1 Chromatographic peaks with characteristic fuel fingerprints eluting between the solvent front and C_{10} indicate the presence of gasoline range. Peaks between C_{10} and C_{25} indicate the presence of diesel range compounds. Patterns that do not resemble either product should be noted.

9.6.2 Product type can be determined by visual inspection of the chromatograms. Chromatograms can become more complicated if crude oil, jet range material, or other refined products are also present. However, it may still be possible to determine that the contamination is due to some sort of petroleum product. Industrial solvents can interfere in the analysis; however, the chromatographic fingerprints would be noticeably different. The best approach to maximize the probability of a correct identification is to analyze reference fuels, from the sample location, along with the sample (if available). These reference fuels can also be used as calibration standards if desired.

9.6.3 As with any gas chromatographic procedure using non-selective flame ionization detection, interferences are possible from coelution of gasoline components with soil contaminants of other sources. Potentially, any compound with similar boiling point and polarity as the hydrocarbons of gasoline-to-diesel range may have retention times within the range of interest and may result in overestimation of the TPH concentration. For example, volatile industrial solvents, cleaners, and naturally occurring compounds not of petroleum origin may interfere with this analysis. It is often possible to recognize the presence of solvents and cleaners since the characteristic fingerprint of gasoline, kerosene, diesel, and heavier materials is altered.

9.6.4 Decisions should be made by the analyst in determination of cutoff points for quantitation of different product ranges when contamination is caused by a combination of sources. For example, if soils are contaminated with gasoline range and diesel range materials, there is an area of overlap where certain components are common to both types of petroleum fractions. A compromise cutoff for mixtures of gasoline with diesel fuel range material is C₁₀. There is no appropriate cutoff for a mixture of jet fuel or kerosene since there is a great deal of overlap. Crude oil contamination also contains a wide range of materials. In cases where mixed products are present, it is perhaps best not to quantitate how much is due to what type of product but to simply quantitate total hydrocarbons and state the approximate carbon range observed.

In order to minimize quantitation problems due to column bleed, the method is best suited for analysis of materials up to diesel range. Heavier materials can be detected with a qualitative identification of product mix but not quantitated effectively.

9.6.5 Additional information on hydrocarbon pattern interpretation is included in some of the references cited [11-13].

9.7 Gas Chromatographic Analysis

- 9.7.1 Samples are analyzed by GC/FID. Suggested injection volumes are 1 to 4 μL using the conditions established in 9.3.
- 9.7.2 After initial calibration (9.5.2) has been performed, verify the calibration by analysis of a mid-point standard at the start of a new analytical sequence using the criteria in 9.5.2.4.
- 9.7.3 For samples that contain unresolved hydrocarbons, baseline projection should be used to generate the area for TPH calculation or for a group within a defined boiling range/carbon number. The GC conditions used for this method produce minimal column bleed up to C_{35} .
- 9.7.4 Alternatively, if peak resolution is adequate, valley-to-valley integration may be used to generate peak areas. This is only possible in the gasoline range (up to C_{12}). The analyst should avoid discarding chromatographic area related to unresolved hydrocarbons.
- 9.7.5 If the product concentration exceeds the linear range of the method in the final extract, the extract should be diluted and reanalyzed. The upper end of the linear range is defined as the highest standard in the calibration curve. The linear range tested is approximately equivalent to 50 $\mu\text{g/mL}$ to 10,000 $\mu\text{g/mL}$ of petroleum hydrocarbons in the extract. Linearity beyond this range should be verified.

9.8 Calculations

- 9.8.1 External Standard Calibration: The concentration of TPH, aliphatic hydrocarbons, aromatic hydrocarbons, selected hydrocarbon ranges, or target analytes in a sample can be calculated from the appropriate area using either calibration factors or regression analysis.

$$C_s = \frac{C_c \times V_t \times D}{W_s} \times \frac{1 \text{ mg}}{1000 \text{ } \mu\text{g}}$$

where:

Cs = Concentration of TPH, hydrocarbon range or specific analytes (mg/kg or mg/L).

Cc = Concentration from calibration curve in $\mu\text{g/mL}$. (If CF is used for calculations, this value is area calibration/CF).

Vt = Volume of extract (mL).

D = Dilution factor, if dilution was performed on the sample prior to analysis. If no dilution was made, $D = 1$, dimensionless.

Ws= Weight of sample extracted (kg). If a water sample, then the units are L.

9.8.2 The peak areas may be divided into desired carbon ranges/boiling point distribution if so desired. Patterns that do not resemble hydrocarbon products should be noted if the analyst is familiar with pattern recognition/fingerprints of petroleum products.

9.9 Calculation of Approximate Boiling Point Distribution: The approximate boiling point distribution is calculated by normalization of sums of peak areas of portions of the chromatograms eluting between preselected retention times as indicated in **Table 1**. Actual retention times should be verified in the laboratory. These retention times correspond to known boiling points selected as references. Characterization by individual approximate carbon number ranges is done up to C₃₅. This is only a guideline. Other markers or groupings can be used. The chromatographic column used in this method is primarily a boiling point, non-polar column. Compound separation is achieved by boiling point differences. A homologous series of n-alkanes is used to approximate boiling point references.

10.0 Quality Control

10.1 General Requirements and Recommendations

10.1.1 The laboratory should establish the ability to generate acceptable accuracy and precision. This should include the analysis of QC check samples plus the calculation of average recovery and the standard deviation of the recovery as outlined in EPA Method 8000B, Section 8.0 [1].

- 10.1.2 The laboratory should, on an ongoing basis, demonstrate through the analysis of quality control check standards that the operation of the measurement system is in control. This should include calibration verification every 10 samples, method blank, LCS, matrix spike, and matrix spike duplicate every 20 samples.
- 10.1.3 After successful calibration (Section 9.5), analyze a reagent blank sample with every analytical batch or sequence. The blank should not have petroleum hydrocarbons above the practical quantitation limit. In addition, n-pentane or methylene chloride solvent blanks should be run after samples suspected of being highly contaminated to determine if sample carryover has occurred.
- 10.1.4 Each laboratory should generate control limits based on the average recovery ± 3 standard deviations. For the LCS, the laboratory must meet the minimum criteria of 60-140% recovery for the whole TPH.
- 10.1.5 If any of the criteria in 10.3 and 10.4 are not met, the problem should be corrected before samples are analyzed.
- 10.1.6 Field blanks, duplicates, and matrix spikes are recommended for specific sampling programs. Matrix spikes should use the spike levels specified for laboratory control samples.
- 10.1.7 Performance evaluation (PE) samples from an independent commercial source for both soil and water samples at both low (5-8 mg/L for water and 50-100 mg/kg for soil) and high (20-50 mg/L for water and 1,000-20,000 mg/kg for soil) levels should be analyzed prior to performing analysis. Data and chromatograms for these PE samples must be kept on file at the laboratory for audit purposes. The performance evaluation samples should be analyzed yearly.

10.2 Minimum Instrument QC

- 10.2.1 The instrument should be able to achieve adequate separation and resolution of peaks and analytes of interest.
- 10.2.2 The n-hexane (nC₆) peak should be adequately resolved from the solvent in the chromatographic run.
- 10.2.3 Retention time windows should be established for each analyte and/or carbon range of interest each time a new GC column is installed, and should be verified and/or adjusted on a daily basis.
- 10.2.4 Calibration curves should be developed based upon the analysis of calibration standards prepared at a minimum of five concentration levels. The linearity of calibration or calibration factors may be assumed if the percent relative standard deviation (% RSD) over the working range of the curve is less than or equal to 25%. Alternatively, if linear regression analysis is used for quantitation, the correlation coefficient (r) should be at least 0.995.
- 10.2.5 In order to demonstrate the absence of mass discrimination, the response ratio of C₃₅ to C₂₀ should be at least 0.80.

10.3 Initial and Periodic Method QC Demonstrations: The following should be conducted as an initial demonstration of laboratory capability, prior to the analysis of any samples. Subsequent to this initial demonstration, additional evaluations of this nature should be conducted on a periodic basis, in response to changes in instrumentation or operations, and/or in response to confirmed or suspected systems, method, or operational problems.

- 10.3.1 Accuracy and Precision: To demonstrate initial laboratory capability, analyze a minimum of four replicate deionized water and clean sand blanks spiked with the TPH standards in Section 7.4.1 or 7.4.2 at approximately 10 to 20 mg/L (water) and 100 to 200 mg/kg (soil).

- 10.3.1.1 Extract and analyze each replicate according to the procedures described in Section 9.0.
 - 10.3.1.2 Calculate the measured concentrations of TPH from nC_6 to nC_{35} in all replicates, the mean accuracy (as a percentage of true value) for each analyte, and the precision (as % RSD) of the measurements for each analyte.
 - 10.3.1.3 For each determination, the mean accuracy, expressed as a percentage of the true value, should be between 60% and 140%.
 - 10.3.1.4 If desired, the accuracy and precision evaluation may be combined with the MDL evaluation specified in Paragraph 10.3.2.
- 10.3.2 Method Detection Limits
- 10.3.2.1 Soil/sediment MDLs are determined by extracting 7-10 replicates of 10 g of clean sand blanks which have been fortified with either of the stock solutions defined in Sections 7.4.1 or 7.4.2 at approximately 50 mg/kg. Extract and analyze each replicate according to the procedures described in Section 9.0. Calculate the Method Detection Limit (MDL) using guidelines in SW-846 [1].
 - 10.3.2.2 Water MDLs are determined by extracting 7-10 replicates of deionized water fortified with stock solution in 7.4.1 or 7.4.2 at approximately 5 mg/L. Extract and analyze each replicate according to the procedure described in section 9.0. Calculate the MDL using guidelines in SW-846 [1].
- 10.3.3 Fractionation: The stock solution described in Section 7.4.2 can be used to demonstrate the capability of properly fractionating aliphatic and aromatic hydrocarbons in a sample.

10.3.3.1 Prepare the column and follow the fractionation as described in Section 9.2 for the fractionation of 1 mL of the stock solution in Section 7.4.2.

NOTE: The amount of n-pentane used during fractionation is critical. Excessive n-pentane will cause elution of aromatics into the aliphatic fraction. Insufficient n-pentane will cause low recoveries of the aliphatic fraction. The volume of n-pentane recommended (8-10 mL) may need to be adjusted to meet QC limits.

10.3.3.2 For each analyte within the fractionation check solution, the mean accuracy, expressed as a percentage of the true value, should be between 60% and 140%.

10.3.3.3 It is acceptable to encounter a 10 to 20% crossover of the fractions. This means that it is within the acceptance criteria of this method to have 10 to 20% aliphatics in the aromatic fraction and 10 to 20% aromatics in the aliphatic fraction.

10.4 Ongoing Method QC Demonstrations

10.4.1 At a minimum, with every batch of 20 samples or less the lab should analyze the following:

10.4.1.1 **Calibration Check Standard:** A mid-range calibration standard, prepared from the same stock standard solution used to develop the calibration curve, should be analyzed prior to sample analysis to verify the calibration state of the instrument. For large analytical batches that contain more than 10 samples, the analysis of an additional mid-range calibration check standard is recommended after the analysis of the 10th sample. If the relative percent difference (RPD) of any analyte within a calibration check standard varies from the predicted response by more than 25%, a new calibration curve should be prepared for that analyte (see Section 9.5).

Any sample analyzed after the last acceptable check standard must be reanalyzed.

10.4.1.2 Laboratory Control Sample: A soil LCS is prepared by fortifying 10 g of a clean sand blank with 0.25 mL to 1.0 mL of one of the standards described in Sections 7.4.1 and 7.4.2 for spiking solutions. A water LCS is prepared by fortifying 30 mL of deionized water with 0.1 mL of standard described in Sections 7.4.1 and 7.4.2. The spike recovery should be between lab-generated control chart limits. If there is insufficient data to control chart the maximum default, limits of 60% to 140% may be used.

10.4.1.3 Matrix Spike (MS) and Matrix Spike Duplicates (MSD): A soil matrix spike is prepared by fortifying an actual sample with 0.25 mL to 1.0 mL of the matrix spiking solution. A soil matrix spike duplicate is prepared the same way as the soil matrix spike. A water matrix spike is prepared by fortifying an actual sample with 0.1 mL of the matrix spiking solution. A water matrix spiked duplicate is prepared the same way as the water matrix spike. The purpose of the matrix spike is to determine whether the sample matrix contributes bias to the analytical results. The purpose of the matrix spike duplicate is to determine the precision of the analysis. The background concentrations of the analytes in the sample matrix should be determined in a separate aliquot and the measured values in the matrix corrected for background concentrations. The corrected concentrations of TPH for the MS spike should be within the lab-generated control limits for the LCS. If there is insufficient data to control chart the maximum default, limits of 60% to 140% may be used. If the MS is outside of the control limits, then the batch it represents should be noted as having

matrix interference. The LCS should be used to show the method is not contributing to spike loss. If the LCS falls outside the lab-generated control limits then that batch needs to be reanalyzed until the LCS falls within the generated control limits. The RPD of the duplicate samples (MS and MSD) should not exceed 30%. If insufficient sample is available for an MS and MSD, then an LCS duplicate must be analyzed. The LCS duplicate recovery must fall within generated control limits. The RPD of the LCS and LCS duplicate must be less than or equal to 30%.

- 10.4.3 If any of the performance standards specified in Section 10.4 are not met, the problem should be corrected before further samples are analyzed. Any samples run between the last QC samples that meet the criteria and those that have fallen out should be rerun. If this is not possible, that data should be reported as suspect.

11.0 Data Production and Reporting

- 11.1 **Calibration:** Using the external calibration procedure (Section 9.5), calibrate the GC as follows:

- 11.1.1 Calculate a collective Calibration Factor (CF), or linear or quadratic regression relationship for the sum of all the peaks that comprise either of the standards defined in Sections 7.4.1 or 7.4.2 for the C₆ to C₃₅ range or a narrower range if the sample contains a smaller carbon range and the option is taken to use a narrower boiling product as a standard. The CF or regression correlation should be done on the total area and the total mass of hydrocarbons in the standard within the specified carbon range.
- 11.1.2 The CF or regression correlation obtained in Section 11.1.1 can be used to calculate the petroleum hydrocarbon concentrations for smaller carbon ranges within the total TPH. These results provide the approximate boiling point distribution/carbon number range information. An easier and more convenient

approach is to calculate the area percents of the individual sums of the peaks within the individual carbon markers ranges normalized with respect to the total area of the C₆ to C₃₅ (TPH area). Then use these percentages to calculate the amounts of petroleum hydrocarbons within those ranges.

11.2 Data Reporting Format

11.2.1 The following information and data should be reported:

11.2.1.1 The sample matrix (soil, sediment, sludge).

11.2.1.2 The date(s) the sample was collected, received by the laboratory, extracted and analyzed.

11.2.1.3 Note in the report if there were any problems observed with the samples as received, such as the physical condition of the containers, the temperature of the samples, and the use of appropriate preservatives. No need to include this information if no problems observed.

11.2.1.4 Moisture content if desired (not required in this method).

11.2.1.5 The calculated concentrations of TPH C₆ to C₃₅ (or whatever carbon range the sample contains), the approximate boiling point/carbon number distribution for the TPH.

11.2.1.6 If sample extract is fractionated, the calculated concentrations of aliphatic and of aromatic hydrocarbons C₆ to C₃₅ (or whatever carbon range the sample contains), the approximate boiling point/carbon number distribution for the fractions.

11.2.1.7 The method reporting limit for the TPH, aliphatic, and aromatic hydrocarbons as well as for the narrower ranges.

11.2.1.8 Chromatograms and data tables.

12.0 Method Performance

- 12.1 The method has been applied to the analysis of neat crude oil, gasoline, JP-4, and diesel. In addition, the method has been used for the analysis of soil samples impacted with crude oil and with petroleum products with different degrees of weathering. Recoveries are typically 80% or better for most samples.
- 12.2 A previous version of this method for TPH and approximate boiling point/carbon number distribution was tested by 12 laboratories. Single operator precision, overall precision and method accuracy were determined and found to be 13%, 30%, and 84%, respectively. A similar study performed on this approach and the fractionation procedure by a single analyst showed an average accuracy of 80% with an average overall RSD of 6%. Also, an independent laboratory evaluation of this method resulted in a single analyst average accuracy of 111% and an overall RSD of 10%.
- 12.3 Additional method refinement and evaluation is in progress.

13.0 Pollution Prevention

- 13.1 The solvent used in this method poses little threat to the environment when recycled and managed properly.
- 13.2 The quantity of chemicals purchased should be based on the expected usage during its shelf life. Standards should be prepared in volumes consistent with laboratory use to minimize the volume of expired standards to be disposed.

14.0 Waste Management

- 14.1 It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management, particularly to comply with the hazardous waste identification rules and land disposal restrictions, and to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is also required.

15.0 References

1. USEPA, "Test Method for the Evaluation of Solid Waste (SW-846)," 3rd Edition (1996).
2. Tong, H.Y., and Karasek, F.W., "Flame Ionization Detector Response Factors for Compound Classes in Quantitative Analysis of Complex Organic Mixtures," Analytical Chemistry, **56**, 2124-2128 (1984).
3. TNRCC TX Method 1005, "Total Petroleum Hydrocarbons," December 1997.
4. API Publication No. 4599, "Interlaboratory Study of Three Methods for Analyzing Petroleum Hydrocarbons in Soils: Diesel-Range Organics (DRO), Gasoline-Range Organics (GRO), Petroleum Hydrocarbons (PHC)," June 1994.
5. American Association of Railroads, "Risk Management Division, Comparison of Analytical Methods for Use in Evaluating the Risk From Petroleum Hydrocarbons in Soil," prepared by Remediation Technologies, Inc., R-903 (1997).
6. Total Petroleum Hydrocarbons Criteria Working Group Series, Volume 3, "Selection of Representative TPH Fractions Based on Fate and Transport Considerations," Amherst Scientific Publishers, July 1997.
7. USEPA Test Method for the Evaluation of Solid Waste (SW-846), Method 3611B, "Alumina Column Cleanup and Separation of Petroleum Wastes" (1996).
8. USEPA Test Method for the Evaluation of Solid Waste (SW-846), Method 3630C, "Silica Gel Cleanup" (1996).
9. Massachusetts Department of Environmental Protection, "Method for the Determination of Extractable Petroleum Hydrocarbons (EPH)" (1995).

10. Washington State WTPH-HCID Method.
11. Rhodes, I.A.L., Olvera, R.Z., Leon, J.L., and Hinojosa, E.M., "Determination of Total Petroleum Hydrocarbons by Capillary Gas Chromatography," Proceedings of the Fourteenth Annual EPA Conference on Analysis of Pollutants in the Environment, Norfolk, Virginia (1991).
12. Rhodes, I.A.L., Hinojosa, E.M., Barker, D.A., and Poole, R.L., "Pitfalls Using Conventional TPH Methods for Source Identification: A Case Study," Proceedings of the Fourteenth Annual EPA Conference on Analysis of Pollutants in the Environment, Norfolk, Virginia (1994).
13. Rhodes, I.A.L., Hinojosa, E.M., Barker, D.A., and Poole, R.L., "Conventional TPH Pitfalls," Environmental Lab, December/January (1995/96).
14. Dempster, H.S., Lollar, B.S., and Feenstra, S., "Tracing Organic Contaminants in Groundwater: A New Methodology Using Compound-Specific Isotopic Analysis," Environmental Science and Technology, **31**, 3193-3197 (1997).
15. ASTM Method D 4547-91, "Standard Practice for Sampling Waste and Soils for Volatile Organics" (1991).

Glossary of Terms

Acute: Rapid. An acute exposure is of short duration.

Aliphatic: Organic compounds which are non-aromatic and non-polar, such as alkanes and alkenes.

Aliquot: A precise portion.

Alkane: A saturated hydrocarbon, containing only hydrogen and carbon in single bonds. Synonymous with saturate fraction, paraffins, and naphthenes.

Alkene: Hydrocarbons containing carbon-carbon double bonds. Alkenes are refinery by-products of the cracking of oils.

Aromatic: Unsaturated (double-bond) cyclic hydrocarbons containing the benzene ring as the basic structural unit of the molecule.

API Gravity: The American Petroleum Institute method for specifying the specific gravity of crude oil.

Benzene Ring: The simplest aromatic compound, containing one, 6-membered carbon ring with double and single carbon-carbon bonds.

Biochemical: Pertaining to the chemistry of biological processes.

Biophysical: Pertaining to the physical nature of biological processes.

Cancer Slope Factor: A conservative estimate of the incremental probability of a person contracting cancer from a unit intake of a chemical over a lifetime.

Carcinogen: A chemical, biologic, or physical agent that can cause cancer.

Chemical of Potential Concern: A chemical that has the potential to negatively impact human health and the environment at a site.

Chronic: Occurring over a long period. Chronic exposures generally occur over a long period of time. USEPA defines chronic exposures as those that may last at least 10% of an average lifetime (i.e., 7 years or more).

Comprehensive Environmental Response and Contingency Liability Act (CERCLA): 1980 United States federal law authorizing identification and remediation of unsupervised hazardous waste sites and spill reporting (also called Superfund).

Detection Limit: The minimum concentration of a chemical that can be detected using a specific measurement procedure and laboratory equipment.

Dose-Response: The measurement of the response of an organism to a dose of chemical.

Eluent: The mobile liquid phase used to separate chemical fractions of oil during liquid chromatography.

Exposure: The means by which receptors come in contact with chemicals.

Exposure Assessment: A three-step process in which the exposure setting is characterized, complete exposure pathways are identified, and the magnitude of the potential exposure is estimated.

Exposure Pathway: The path that a chemical takes from its source to a receptor.

Fingerprint: A chromatographic signature. Can be used for qualitative or quantitative comparisons of the composition of oils.

Fractionation, TPH: The separation of the hydrocarbon extract into compound classes such as aliphatic and aromatic hydrocarbons.

Gas Chromatography: The separation of mixtures of compounds by partition between a mobile gas phase and a stationary liquid phase.

Granuloma: A growth or tumor that appears granulated.

Hazard Identification: A review of site assessment data and the identification of chemicals that may be present at the site and may be of concern.

Hazard Quotient: The ratio of an estimated long-term daily exposure level to an acceptable exposure level. A Hazard Quotient of 1 or less is deemed to be acceptable by the United States Environmental Protection Agency.

Hematological: Pertaining to the blood system.

Hepatotoxicity: Liver toxicity.

Hepatic: Pertaining to the liver.

Indigenous: Naturally-occurring.

Intervention Value: As defined by the Dutch government, the concentration above which soils are considered to be seriously contaminated.

Lacustrine: Pertaining to, produced by, or formed in a lake. Some crude oils originate from lacustrine source rocks.

Leaching Factor: A factor that will predict the amount of contaminant that will partition between soil and water.

Nephrotoxicity: Kidney toxicity.

Non-Aqueous Phase Liquid: A liquid other than water that exists in the subsurface environment.

Non-Carcinogen: A chemical that is not expected to cause cancer, but may cause other adverse health effects.

Oil and Grease: Measurement of the amount of relatively non-volatile hydrocarbons (as well as vegetable oils, animal fats, waxes soaps, greases, and related matter). An aqueous or solid sample measured by gravimetric analysis of a solvent extract.

Oral Cancer Slope Factor: See *Cancer Slope Factor*.

Pathway: See Exposure Pathway.

Phytoavailable: Available for uptake into the tissues of plants.

Phytotoxic: Adverse effects of chemicals on plants.

Polar Compound: An organic compound with distinct regions of partial positive and negative charge. Polar compounds include alcohols and aromatics.

Polyaromatic Hydrocarbon (Polycyclic Aromatic Hydrocarbons): A hydrocarbon that contains more than one benzene ring.

Polynuclear Aromatic: See *Polyaromatic Hydrocarbon*.

Preliminary Remediation Goal: As defined by the United States Environmental Protection Agency Region IX, a risk-based concentration of a chemical in an environmental medium (e.g., soil, water, or air) that is considered to be protective of human health and that can be used as a screening level for evaluating contaminant levels at individual sites, as appropriate.

Protective Concentration Level: As defined by the Texas Natural Resources Conservation Commission, the concentration of a chemical of concern which can remain within the source medium and not result in levels which exceed the applicable human health risk-based exposure limit or ecological protective concentration level at the point of exposure for that exposure pathway.

Receptor: A human being or other organism that has the potential to be exposed to chemicals.

Reference Concentration: An estimate of continuous inhalation exposure to a chemical that is likely to be without an appreciable risk of adverse effect over a lifetime.

Reference Dose: An estimate of daily exposure to a chemical that is likely to be without an appreciable risk of adverse effect over a lifetime.

Residual: The presence of a free product or oil in soil; also called separate-phase hydrocarbons.

Resource Conservation and Recovery Act (RCRA): Legislation that was enacted in the United States in 1976 to regulate solid waste and resource recovery for all but a few exempt wastes.

Risk-Based Corrective Action: A tiered decision-making approach for site assessment, risk assessment, and site management.

Risk-Based Decision-Making: A decision-making approach to site management based on an evaluation of the risks that a given situation might present.

Risk-Based Screening Levels: Chemical-specific concentrations in environmental media that are considered to be protective of human health and the environment.

Risk Characterization: The final step of a risk evaluation, which combines the results of the exposure and toxicity assessments in order to quantify the potential risks to human health and the environment.

Saturated Hydrocarbon: A hydrocarbon that includes normal and branched alkanes and cycloalkanes (paraffins and naphthenes). Saturates are the non-aromatic hydrocarbon fraction of an oil.

Site Specific Target Level (SSTL): As defined by the American Society for Testing and Materials, a risk-based remedial action target level for chemical(s) of concern developed for a particular site under the Tier 2 and Tier 3 evaluations.

Soil Screening Level: As developed by the United States Environmental Protection Agency, a risk-based concentration of a chemical in soil that is protective for potential human health impacts.

Target Value: As defined by the Dutch government, the concentration of a chemical in soil that is considered to be desirable and is generally based on background concentrations of chemicals in soil in the Netherlands.

Total Organic Carbon: The quantity of organic carbon in a solid or aqueous sample as measured by wet oxidation of the sample.

Total Petroleum Hydrocarbon: The quantity of extractable compounds detected in a sample of soil or water as measured by the detection methods (GC, infrared, gravimetric) in a solvent extract of soil or water.

Toxicology: The study of the harmful effects of chemicals on organisms.

Toxicity Assessment: An evaluation of a chemical for its ability to cause cancer or other adverse health effects.

Unsaturated Hydrocarbon: A hydrocarbon containing one or more double or triple bonds, such as alkenes.

Unsaturated Soil: A soil having pore spaces that are not completely filled with water or other fluids.

Volatilization Factor: A factor that predicts the amount of contaminant that will partition between the soil and air.